GEL ORGANOSOL INCLUDING AMPHIPATHIC COPOLYMERIC BINDER HAVING HYDROGEN BONDING FUNCTIONALITY AND LIQUID TONERS FOR ELECTROPHOTOGRAPHIC APPLICATIONS

FIELD OF THE INVENTION

The present invention relates to liquid toner compositions having utility in electrophotography. More particularly, the invention relates to amphipathic copolymer binder particles provided in a gel composition.

BACKGROUND OF THE INVENTION

In electrophotographic and electrostatic printing processes (collectively electrographic processes), an electrostatic image is formed on the surface of a photoreceptive element or dielectric element, respectively. The photoreceptive element or dielectric element may be an intermediate transfer drum or belt or the substrate for the final toned image itself, as described by Schmidt, S. P. and Larson, J. R. in Handbook of Imaging Materials Diamond, A. S., Ed: Marcel Dekker: New York; Chapter 6, pp 227-252, and U.S. Pat. Nos. 4,728,983, 4,321,404, and 4,268,598.

In electrostatic printing, a latent image is typically formed by (1) placing a charge image onto a dielectric element (typically the receiving substrate) in selected areas of the element with an electrostatic writing stylus or its equivalent to form a charge image, (2) applying toner to the charge image, and (3) fixing the toned image. An example of this type of process is described in U.S. Pat. No. 5,262,259.

In electrophotographic printing, also referred to as xerography, electrophotographic technology is used to produce images on a final image receptor, such as paper, film, or the like. Electrophotographic technology is incorporated into a wide range of equipment including photocopiers, laser printers, facsimile machines, and the like.

Electrophotography typically involves the use of a reusable, light sensitive, temporary image receptor, known as a photoreceptor, in the process of producing an electrophotographic image on a final, permanent image receptor. A representative electrophotographic process, discharged area development, involves a series of steps to

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produce an image on a receptor, including charging, exposure, development, transfer, fusing, cleaning, and erasure.

In the charging step, a photoreceptor is substantially uniformly covered with charge of a desired polarity to achieve a first potential, either negative or positive,

5   typically with a corona or charging roller. In the exposure step, an optical system, typically a laser scanner or diode array, forms a latent image by selectively discharging the charged surface of the photoreceptor to achieve a second potential in an imagewise manner corresponding to the desired image to be formed on the final image receptor. In the development step, toner particles of the appropriate polarity are generally brought

10   into contact with the latent image on the photoreceptor, typically using a developer electrically-biased to a potential of the same polarity as the toner polarity and intermediate in potential between the first and second potentials. The toner particles migrate to the photoreceptor and selectively adhere to the latent image via electrostatic forces, forming a toned image on the photoreceptor.

15   In the transfer step, the toned image is transferred from the photoreceptor to the desired final image receptor; an intermediate transfer element is sometimes used to effect transfer of the toned image from the photoreceptor with subsequent transfer of the toned image to a final image receptor. The image may be transferred by physical pressure and contact of the toner, with selective adhesion to a target intermediate or final image

20   receptor as compared to the surface from which it is transferred. Alternatively, the toner may be transferred in a liquid system optionally using an electrostatic assist as discussed in more detail below. In the fusing step, the toned image on the final image receptor is heated to soften or melt the toner particles, thereby fusing the toned image to the final receptor. An alternative fusing method involves fixing the toner to the final receptor

25   under pressure with or without heat. In the cleaning step, residual toner remaining on the photoreceptor is removed.

Finally, in the erasing step, the photoreceptor charge is reduced to a substantially uniformly low value by exposure to light of a particular wavelength band, thereby removing remnants of the original latent image and preparing the photoreceptor for the

30   next imaging cycle.

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Two types of toner are in widespread, commercial use: liquid toner and dry toner. The term "dry" does not mean that the dry toner is totally free of any liquid constituents, but connotes that the toner particles do not contain any significant amount of solvent, e.g., typically less than 10 weight percent solvent (generally, dry toner is as dry as is

5   reasonably practical in terms of solvent content), and are capable of carrying a triboelectric charge. This distinguishes dry toner particles from liquid toner particles.

A typical liquid toner composition generally includes toner particles suspended or dispersed in a liquid carrier. The liquid carrier is typically nonconductive dispersant, to avoid discharging the latent electrostatic image. Liquid toner particles are generally

10   solvated to some degree in the liquid carrier (or carrier liquid), typically in more than 50 weight percent of a low polarity, low dielectric constant, substantially nonaqueous carrier solvent. Liquid toner particles are generally chemically charged using polar groups that dissociate in the carrier solvent, but do not carry a triboelectric charge while solvated and/or dispersed in the liquid carrier. Liquid toner particles are also typically smaller

15   than dry toner particles. Because of their small particle size, ranging from sub-micron to about 5 microns, liquid toners are capable of producing very high-resolution toned images.

A typical toner particle for a liquid toner composition generally comprises a visual enhancement additive (for example, a colored pigment particle) and a polymeric

20   binder. The polymeric binder fulfills functions both during and after the electrophotographic process. With respect to processability, the character of the binder impacts charging and charge stability, flow, and fusing characteristics of the toner particles. These characteristics are important to achieve good performance during development, transfer, and fusing. After an image is formed on the final receptor, the

25   nature of the binder (e.g. glass transition temperature, melt viscosity, molecular weight) and the fusing conditions (e.g. temperature, pressure and fuser configuration) impact durability (e.g. blocking and erasure resistance), adhesion to the receptor, gloss, and the like.

Polymeric binder materials suitable for use in liquid toner particles typically

30   exhibit glass transition temperatures of about -24°C to 55°C, which is lower than the range of glass transition temperatures (50-100°C) typical for polymeric binders used in

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dry toner particles. In particular, some liquid toners are known to incorporate polymeric binders exhibiting glass transition temperatures (T_g) below room temperature (25°C) in order to rapidly self fix, e.g. by film formation, in the liquid electrophotographic imaging process; see e.g. U.S. 6,255,363. However, such liquid toners are also known to exhibit

5   inferior image durability resulting from the low T_g (e.g. poor blocking and erasure resistance). In addition, such toners, while suitable for transfer processes involving contact adhesive forces, are generally unsuitable for transfer processes involving an electrostatic transfer assist due to the extreme tackiness of the toner films after fusing the toned image to a final image receptor. Also low T_g toners are more sensitive to cohesive

10   transfer failure (film split), and are more difficult to clean (sticky) from photoreceptors or intermediate transfer elements.

        In other printing processes using liquid toners, self-fixing is not required. In such a system, the image developed on the photoconductive surface is transferred to an intermediate transfer belt ("ITB") or intermediate transfer member ("ITM") or directly to

15   a print medium without film formation at this stage. See, for example, U.S. Patent Nos. 5,410,392 to Landa, issued on April 25, 1995; and 5,115,277 to Camis, issued on May 19, 1992. In such a system, this transfer of discrete toner particles in image form is carried out using a combination of mechanical forces, electrostatic forces, and thermal energy. In the system particularly described in the '277 patent, DC bias voltage is

20   connected to an inner sleeve member to develop electrostatic forces at the surface of the print medium for assisting in the efficient transfer of color images.

        The toner particles used in such a system have been previously prepared using conventional polymeric binder materials, and not polymers made using an organosol process (described in more detail below). Thus, for example the '392 patent states that

25   the liquid developer to be used in the disclosed system is described in U. S. Patent No. 4,794,651 to Landa, issued on December 27, 1988. This patent discloses liquid toners made by heating a preformed high T_g polymer resin in a carrier liquid to an elevated temperature sufficiently high for the carrier liquid to soften or plasticize the resin, adding a pigment, and exposing the resulting high temperature dispersion to a high energy

30   mixing or milling process.

Although such non self-fixing liquid toners using higher T_g (T_g generally greater than or equal to about 60°C) polymeric binders should have good image durability, such toners are known to exhibit other problems related to the choice of polymeric binder, including image defects due to the inability of the liquid toner to rapidly self fix in the imaging process, poor charging and charge stability, poor stability with respect to agglomeration or aggregation in storage, poor sedimentation stability in storage, and the requirement that high fusing temperatures of about 200-250°C be used in order to soften or melt the toner particles and thereby adequately fuse the toner to the final image receptor.

To overcome the durability deficiencies, polymeric materials selected for use in both nonfilm-forming liquid toners and dry toners more typically exhibit a range of T_g of at least about 55-65°C in order to obtain good blocking resistance after fusing, yet typically require high fusing temperatures of about 200-250°C in order to soften or melt the toner particles and thereby adequately fuse the toner to the final image receptor. High fusing temperatures are a disadvantage for dry toners because of the long warm-up time and higher energy consumption associated with high temperature fusing, and because of the risk of fire associated with fusing toner to paper at temperatures above the autoignition temperature of paper (233°C).

In addition, some liquid and dry toners using high T_g polymeric binders are known to exhibit undesirable partial transfer (offset) of the toned image from the final image receptor to the fuser surface at temperatures above or below the optimal fusing temperature, requiring the use of low surface energy materials in the fuser surface or the application of fuser oils to prevent offset. Alternatively, various lubricants or waxes have been physically blended into the dry toner particles during fabrication to act as release or slip agents; however, because these waxes are not chemically bonded to the polymeric binder, they may adversely affect triboelectric charging of the toner particle or may migrate from the toner particle and contaminate the photoreceptor, an intermediate transfer element, the fuser element, or other surfaces critical to the electrophotographic process.

In addition to the polymeric binder and the visual enhancement additive, liquid toner compositions can optionally include other additives. For example, charge control

agents can be added to impart an electrostatic charge on the toner particles. Dispersing agents can be added to provide colloidal stability, aid fixing of the image, and provide charged or charging sites for the particle surface. Dispersing agents are commonly added to liquid toner compositions because toner particle concentrations are high (inter-particle distances are small) and electrical double-layer effects alone will not adequately stabilize the dispersion with respect to aggregation or agglomeration. Release agents can also be used to help prevent the toner from sticking to fuser rolls when those are used. Other additives include antioxidants, ultraviolet stabilizers, fungicides, bactericides, flow control agents, and the like.

One fabrication technique involves synthesizing an amphipathic copolymeric binder dispersed in a liquid carrier to form an organosol, then mixing the formed organosol with other ingredients to form a liquid toner composition. Typically, organosols are synthesized by nonaqueous dispersion polymerization of polymerizable compounds (e.g. monomers) to form copolymeric binder particles that are dispersed in a low dielectric hydrocarbon solvent (carrier liquid). These dispersed copolymer particles are sterically-stabilized with respect to aggregation by chemical bonding of a steric stabilizer (e.g. graft stabilizer), solvated by the carrier liquid, to the dispersed core particles as they are formed in the polymerization. Details of the mechanism of such steric stabilization are described in Napper, D.H., "Polymeric Stabilization of Colloidal Dispersions," Academic Press, New York, N.Y., 1983. Procedures for synthesizing self-stable organosols are described in "Dispersion Polymerization in Organic Media," K.E.J. Barrett, ed., John Wiley: New York, N.Y., 1975.

Liquid toner compositions have been manufactured using dispersion polymerization in low polarity, low dielectric constant carrier solvents for use in making relatively low glass transition temperature $(T_g \leq 30^{\circ}C)$ film-forming liquid toners that undergo rapid self-fixing in the electrophotographic imaging process. See, e.g., U.S. Pat. No. 5,886,067 and 6,103,781. Organosols have also been prepared for use in making intermediate glass transition temperature $(T_g$ between 30-55$^{\circ}C)$ liquid electrostatic toners for use in electrostatic stylus printers. See, e.g., U.S. Pat. No. 6,255,363 B1. A representative non-aqueous dispersion polymerization method for forming an organosol is a free radical polymerization carried out when one or more ethylenically-unsaturated

monomers, soluble in a hydrocarbon medium, are polymerized in the presence of a preformed, polymerizable solution polymer (e.g. a graft stabilizer or "living" polymer). See U.S. Pat. No. 6,255,363.

Once the organosol has been formed, one or more additives can be incorporated, as desired. For example, one or more visual enhancement additives and/or charge control agents can be incorporated. The composition can then subjected to one or more mixing processes, such as homogenization, microfluidization, ball-milling, attritor milling, high energy bead (sand) milling, basket milling or other techniques known in the art to reduce particle size in a dispersion. The mixing process acts to break down aggregated visual enhancement additive particles, when present, into primary particles (having a diameter in the range of 0.05 to 1.0 microns) and may also partially shred the dispersed copolymeric binder into fragments that can associate with the surface of the visual enhancement additive.

According to this embodiment, the dispersed copolymer or fragments derived from the copolymer then associate with the visual enhancement additive, for example, by adsorbing to or adhering to the surface of the visual enhancement additive, thereby forming toner particles. The result is a sterically-stabilized, nonaqueous dispersion of toner particles having a size in the range of about 0.1 to 2.0 microns, with typical toner particle diameters in the range 0.1 to 0.5 microns. In some embodiments, one or more charge control agents can be added before or after mixing, if desired.

Several characteristics of liquid toner compositions are important to provide high quality images. Toner particle size and charge characteristics are especially important to form high quality images with good resolution. Further, rapid self-fixing of the toner particles is an important requirement for some liquid electrophotographic printing applications, e.g. to avoid printing defects (such as smearing or trailing-edge tailing) and incomplete transfer in high-speed printing. For example, in organosol toner compositions that exhibit low T_gs, the resulting film that is formed during the imaging process may be sticky and cohesively weak under transfer conditions. This may result in image splitting or undesired residue left on the photoreceptor or intermediate image receptor surfaces.

Another important consideration in formulating a liquid toner composition relates to the durability and archivability of the image on the final receptor. Erasure resistance, e.g.

resistance to removal or damage of the toned image by abrasion, particularly by abrasion from natural or synthetic rubber erasers commonly used to remove extraneous pencil or pen markings, is a desirable characteristic of liquid toner particles.

Another important consideration in formulating a liquid toner is the tack of the image on the final receptor. It is desirable for the image on the final receptor to be essentially tack-free over a fairly wide range of temperatures. If the image has a residual tack, then the image can become embossed or picked off when placed in contact with another surface (also referred to as blocking). This is particularly a problem when printed sheets are placed in a stack. Resistance of the image on the final image receptor to damage by blocking to the receptor (or to other toned surfaces) is another desirable characteristic of liquid toner particles.

To address this concern, a film laminate or protective layer may be placed over the surface of the image. This laminate often acts to increase the effective dot gain of the image, thereby interfering with the color rendition of a color composite. In addition, lamination of a protective layer over a final image surface adds both extra cost of materials and extra process steps to apply the protective layer, and may be unacceptable for certain printing applications (e.g. plain paper copying or printing).

Various methods have been used to address the drawbacks caused by lamination. For example, approaches have employed radiation or catalytic curing methods to cure or crosslink the liquid toner after the development step in order to eliminate tack. Such curing processes are generally too slow for use in high speed printing processes. In addition, such curing methods can add significantly to the expense of the printing process. The curable liquid toners frequently exhibit poor self stability and can result in brittleness of the printed ink.

Another method to improve the durability of liquid toned images and address the drawbacks of lamination is described in U.S. Patent No. 6,103,781. U.S. Patent No. 6,103,781 describes a liquid ink composition containing organosols having side-chain or main-chain crystallizable polymeric moieties. At column 6, lines 53 - 60, the authors describe a binder resin that is an amphipathic copolymer dispersed in a liquid carrier (also known as an organosol) that includes a high molecular weight (co)polymeric steric stabilizer covalently bonded to an insoluble, thermoplastic (co)polymeric core. The steric

stabilizer includes a crystallizable polymeric moiety that is capable of independently and reversibly crystallizing at or above room temperature (22°C).

According to the authors, superior stability of the dispersed toner particles with respect to aggregation is obtained when at least one of the polymers or copolymers

5   (denoted as the stabilizer) is an amphipathic substance containing at least one oligomeric or polymeric component having a weight-average molecular weight of at least 5,000 which is solvated by the liquid carrier. In other words, the selected stabilizer, if present as an independent molecule, would have some finite solubility in the liquid carrier. Generally, this requirement is met if the absolute difference in Hildebrand solubility

10   parameter between the steric stabilizer and the solvent is less than or equal to 3.0 $MPa^{1/2}$.

As described in U.S. Patent No. 6,103,781, the composition of the insoluble resin core is preferentially manipulated such that the organosol exhibits an effective glass transition temperature (T_g) of less than 22°C, more preferably less than 6°C. Controlling the glass transition temperature allows one to formulate an ink composition containing

15   the resin as a major component to undergo rapid film formation (rapid self-fixing) in liquid electrophotographic printing or imaging processes using offset transfer processes carried out at temperatures greater than the core T_g. Preferably, the offset transfer process is carried out at a temperature at or above 22°C. (Column 10, lines 36-46). The presence of the crystallizable polymeric moiety that is capable of independently and

20   reversibly crystallizing at or above room temperature (22°C) acts to protect the soft, tacky, low T_g insoluble resin core after fusing to the final image receptor. This acts to improve the blocking and erasure resistance of the fused, toned image at temperatures up to the crystallization temperature (melting point) of the crystallizable polymeric moiety.

Liquid inks using gel organosol compositions have been described in US Patent

25   No. 6,255,363, and also in WO 01/79316, WO 01/79363, and WO 01/79364. These systems are designed to provide toner compositions that will form films at room temperature and without specific drying procedures or heating elements. See, for example the US '363 patent at column 15, lines 50-63. Thus, the T_g of the toner materials described in these patents and applications specifically are described to be low

30   as part of ability to form a film at room temperature.

SUMMARY OF THE INVENTION

The present invention relates to gel liquid electrophotographic toner compositions comprising a liquid carrier and toner particles dispersed in the liquid carrier. The liquid carrier has a Kauri-butanol number less than 30 mL. The toner particles comprise a polymeric binder comprising at least one amphipathic copolymer with one or more S material portions and one or more D material portions. The toner composition comprises hydrogen bonding functionality in an amount sufficient to provide a three dimensional gel of controlled rigidity which can be reversibly reduced to a fluid state by application of energy. The electrophotographic toner composition substantially does not form a film under Photoreceptor Image Formation conditions.

For purposes of the present invention, a "gel" is a three dimensional matrix of controlled rigidity which can be reversibly reduced to a fluid state by application of energy. Gel formation in particular is believed to result from particle-particle interactions that cause reversible agglomeration of the particles. These particle-particle interactions, however, are weak enough to be broken down by the application of shear energy, sonic energy, heat energy, and/or the like.

As noted above, the compositions of the present invention are formulated so that the toner substantially does not form a film under Photoreceptor Image Formation conditions, as defined below. Because of the unique formulation, essentially no film is formed on the photoconductor during the printing process. Instead, the image is transferred from the surface of a photoconductor to an intermediate transfer material or directly to a print medium without substantial film formation on the photoconductor. Film formation may occur after transfer from the photoconductor, preferably at or before the time of final fusing of the image on the final receptor.

"Photoreceptor Image Formation conditions" for purposes of the present invention means that a composition substantially does not form a film when at a solids content of from about 30% to about 40%, and at a temperature between 23°C and 45°C, and more preferably does not form a film when at a solids content of less than 70% at a temperature between 23°C and 45°C. As a primary consideration, the T_g of the amphipathic polymer strongly influences whether a film is formed by the organosol gel

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composition of the present invention. Additional factors, however, may be brought to bear to influence the film formation properties of the composition, such as selection of carrier solvent, location of homogenous regions of polymer components having lower or higher T_g as compared to the balance of the amphipathic copolymer, and the

5   incorporation of various functional groups, particularly at the S material portion of the amphipathic copolymer. The skilled artisan is able to prepare organosol compositions meeting such identified film forming properties by manipulation of these and other factors that will be understood in the art.

Gel toner compositions that do not substantially form a film under Photoreceptor

10   Image Formation conditions provide specific advantages, including excellent image transfer from the photoreceptor, with low or no back transfer of the image to the photoreceptor during the printing process. Additionally, the gel toner compositions exhibit exceptional storage stability without the need to incorporate dispersant, surfactant, or stabilizer additives in an amount deleterious to image quality, although these

15   additional components can be used if desired. Because amphipathic copolymers are used, the S portion of the copolymer may easily comprise covalently bonded stabilizing functionalities that further assist in stabilization of the overall liquid toner composition. Superior final image properties are also observed relative to erasure resistance and blocking resistance.

20   Additionally, toner particles comprising the amphipathic copolymers as described herein are consistent in size and shape, and therefore provide substantial benefit in uniformity in image formation. Such uniformity of size and shape is difficult or impossible to achieve in conventionally milled toner binder polymers. The liquid toner compositions according to the invention provide a system wherein an image can

25   surprisingly be provided having excellent image transfer, and additionally are resistant to blocking. Images made using the compositions of the present invention are surprisingly non-tacky and are resistant to marring and undesired erasure. The gels impart useful properties to the liquid ink, notably improved sedimentation stability of the colorant, without compromising print quality or ink transfer performance. The inks formulated

30   with the gels also exhibit improved redispersion characteristics upon settling, and do not form dilatant sediments such as those formed by non-gelled organosol inks. These

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characteristics of gel inks facilitate preparation and use of high solids ink concentrates (greater than 2% by weight solids, more preferably greater than 10% by weight solids, and most preferably >20%), thus providing an increased number of printed pages or images from a given volume of ink. Surprisingly, the organosols of the present invention exhibit effectively larger particle size of gels, thereby exhibiting low to intermediate charge per mass (Q/M) suitable for high optical density development, but additionally exhibiting a break up of the gel under image development field to yield fine particles for high resolution imaging.

As used herein, the term "amphipathic" refers to a copolymer having a combination of portions having distinct solubility and dispersibility characteristics in a desired liquid carrier that is used to make the copolymer and/or used in the course of preparing the liquid toner particles. Preferably, the liquid carrier (also sometimes referred to as "carrier liquid") is selected such that at least one portion (also referred to herein as S material or block(s)) of the copolymer is more solvated by the carrier while at least one other portion (also referred to herein as D material or block(s)) of the copolymer constitutes more of a dispersed phase in the carrier.

The gel is formed by incorporating an amount of hydrogen-bond donor functionality and hydrogen bond acceptor functionality in the amphipathic copolymer in an amount sufficient to form a gel. The hydrogen bonding functionalities may be provided in the S material portion, in the D material portion, or in both the S material portion and D material portion of the amphipathic copolymer. The hydrogen bonding functionalities form weak, reversible intermolecular hydrogen bonds between dispersed amphipathic copolymer particles, thereby forming a gel organosol.

In an alternative embodiment of the present invention, the amphipathic copolymer is optionally provided with only hydrogen-bond donor functionality or hydrogen bond acceptor functionality, and an additional bridging compound having at least two of the opposite of hydrogen-bond donor functionality or hydrogen bond acceptor functionality is provided in the organosol composition. For example, if the amphipathic copolymer is provided with only hydrogen-bond acceptor functionality, the bridging compound has at least two hydrogen bond donor functionalities. The hydrogen bonding functionalities on the amphipathic copolymer form weak, reversible intermolecular non-covalent bonds

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with the corresponding the hydrogen bonding functionalities on the bridging compound, thereby forming a gel organosol.

The gel organosols provide a new approach to improving the sedimentation and redispersion properties of pigmented inks. The method of inducing gelation does not require manipulation of the relative difference in solubility parameter between the amphipathic copolymer and the carrier solvent into a range (solubility parameter difference greater than 2.5 MPa$^{1/2}$) that acts to reduce agglomeration stability of the amphipathic copolymer. This allows the ink formulator increased flexibility in selection of monomer components of the amphipathic copolymer, as well as greater flexibility in carrier fluid selection.

For example, side-chain crystallizable monomers that have a high degree of solubility in the carrier solvent may be incorporated into the amphipathic copolymer without sacrificing gelation characteristics. The use of crystallizable polymeric moieties to improve the durability of non-gel organosol inks has been disclosed in U.S. 5,886,067. Heretofore, the use of such crystallizable polymeric moieties at high weight percentages in an amphipathic copolymer has prevented the formation of gel organosols owing to the relative solubility parameter difference between the amphipathic copolymer and the carrier solvent falling in the range of good solubility (0-2.5 MPa$^{1/2}$). It would be advantageous to combine the characteristics of a gel organosol and a controlled-crystallinity organosol into a single composition. Preferably, the toner particles additionally comprise at least one visual enhancement additive.

In preferred embodiments, the copolymer is polymerized in situ in the desired liquid carrier. The use of the carrier liquid as the reaction solvent facilitates the formation of substantially monodisperse copolymeric particles suitable for use in toner compositions. The resulting organosol is then preferably mixed with at least one visual enhancement additive and optionally one or more other desired ingredients to form a liquid toner. During such combination, ingredients comprising the visual enhancement particles and the copolymer will tend to self-assemble into composite particles having solvated (S) portions and dispersed (D) portions. Specifically, it is believed that the D material of the copolymer will tend to physically and/or chemically interact with the

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surface of the visual enhancement additive, while the S material helps promote dispersion in the carrier.

DETAILED DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS

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The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather, the embodiments are chosen and described so that others

10 skilled in the art can appreciate and understand the principles and practices of the present invention.

Preferably, the nonaqueous liquid carrier of the organosol is selected such that at least one portion (also referred to herein as the S material or portion) of the amphipathic copolymer is more solvated by the carrier while at least one other portion (also referred to

15 herein as the D material or portion) of the copolymer constitutes more of a dispersed phase in the carrier. In other words, preferred copolymers of the present invention comprise S and D material having respective solubilities in the desired liquid carrier that are sufficiently different from each other such that the S blocks tend to be more solvated by the carrier while the D blocks tend to be more dispersed in the carrier. More

20 preferably, the S blocks are soluble in the liquid carrier while the D blocks are insoluble. In particularly preferred embodiments, the D material phase separates from the liquid carrier, forming dispersed particles.

From one perspective, the polymer particles when dispersed in the liquid carrier may be viewed as having a core/shell structure in which the D material tends to be in the

25 core, while the S material tends to be in the shell. The S material thus functions as a dispersing aid, steric stabilizer or graft copolymer stabilizer, to help stabilize dispersions of the copolymer particles in the liquid carrier. Consequently, the S material may also be referred to herein as a "graft stabilizer." The core/shell structure of the binder particles tends to be retained when the particles are dried when incorporated into liquid toner

30 particles.

The solubility of a material, or a portion of a material such as a copolymeric portion, may be qualitatively and quantitatively characterized in terms of its Hildebrand

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solubility parameter. The Hildebrand solubility parameter refers to a solubility parameter represented by the square root of the cohesive energy density of a material, having units of $(\text{pressure})^{1/2}$, and being equal to $(\Delta H - RT)^{1/2} / V^{1/2}$, where ΔH is the molar vaporization enthalpy of the material, R is the universal gas constant, T is the absolute temperature,

5 and V is the molar volume of the solvent. Hildebrand solubility parameters are tabulated for solvents in Barton, A. F. M., <u>Handbook of Solubility and Other Cohesion Parameters</u>, 2d Ed. CRC Press, Boca Raton, Fla., (1991), for monomers and representative polymers in <u>Polymer Handbook</u>, 3rd Ed., J. Brandrup & E. H. Immergut, Eds. John Wiley, N.Y., pp 519-557 (1989), and for many commercially available polymers in Barton, A. F. M.,

10 <u>Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters</u>, CRC Press, Boca Raton, Fla., (1990).

The degree of solubility of a material, or portion thereof, in a liquid carrier may be predicted from the absolute difference in Hildebrand solubility parameters between the material, or portion thereof, and the liquid carrier. A material, or portion thereof, will be

15 fully soluble or at least in a highly solvated state when the absolute difference in Hildebrand solubility parameter between the material, or portion thereof, and the liquid carrier is less than approximately $1.5 \text{ MPa}^{1/2}$. On the other hand, when the absolute difference between the Hildebrand solubility parameters exceeds approximately 3.0 $\text{MPa}^{1/2}$, the material, or portion thereof, will tend to phase separate from the liquid

20 carrier, forming a dispersion. When the absolute difference in Hildebrand solubility parameters is between $1.5 \text{ MPa}^{1/2}$ and $3.0 \text{ MPa}^{1/2}$, the material, or portion thereof, is considered to be weakly solvatable or marginally insoluble in the liquid carrier. While not being bound by theory, it is believed that the amphipathic copolymer is hydrogen bonded to such an extent that it behaves as an extremely high molecular weight

25 copolymer near its incipient phase separation point in the dispersant liquid.

Gel organosols are dispersions in which the attractive interactions between the elements of the dispersed phase are so strong that the whole system develops a rigid network structure and, under small stresses, behaves elastically. The characteristic of organosol gelation is visibly apparent to one skilled in the art. The hydrogen bonded

30 organosols rapidly gel to form a voluminous polymer sediment and a substantially clear supernatant layer of carrier liquid upon standing.

While not being bound by theory, it is believed that gelation of the amphipathic copolymer organosol is induced by forming hydrogen bonds between portions of an amphipathic copolymer. The hydrogen-bonding polymerizable compounds may be incorporated in the S material portion, the D material portion, or in both the S material portion and the D material portion. It is also possible to prepare two separate and distinct amphipathic copolymer compositions, each including one or more hydrogen-bonding polymerizable compounds in the S material portion, the D material portion, or both. In a preferred embodiment one organosol composition would be prepared with hydrogen-bond donor functionality, and another organosol composition would be prepared with hydrogen bond acceptor functionality. In this embodiment, gelation would not occur until the two organosols were blended together in amount sufficient to initiate gelation of the composition.

The composition may also be provided with an additional polyfunctional bridging compound having at least two of hydrogen bonding functionalities to assist in gel formation. Optionally, this additional polyfunctional bridging compound is provided with only hydrogen bond acceptor functionality together with amphipathic copolymers having only hydrogen bond donor functionality, or may be provided with only hydrogen bond donor functionality together with amphipathic copolymers having only hydrogen bond acceptor functionality.

The strength of the gel (and hence sedimentation resistance of the ink) can be readily manipulated by controlling the extent to which the amphipathic copolymer is hydrogen-bonded. Greater gel strength (greater sedimentation resistance) is obtained by increasing the density of hydrogen bonding functionality (percentage of hydrogen-bonding polymerizable compound) of the amphipathic copolymer.

Because the Hildebrand solubility of a material may vary with changes in temperature, such solubility parameters are preferably determined at a desired reference temperature such as at 25°C.

Those skilled in the art understand that the Hildebrand solubility parameter for a copolymer, or portion thereof, may be calculated using a volume fraction weighting of the individual Hildebrand solubility parameters for each monomer comprising the copolymer, or portion thereof, as described for binary copolymers in Barton A. F. M.,

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Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton, p 12 (1990). The magnitude of the Hildebrand solubility parameter for polymeric materials is also known to be weakly dependent upon the weight average molecular weight of the polymer, as noted in Barton, pp 446-448. Thus, there will be a preferred

5   molecular weight range for a given polymer or portion thereof in order to achieve desired solvating or dispersing characteristics. Similarly, the Hildebrand solubility parameter for a mixture may be calculated using a volume fraction weighting of the individual Hildebrand solubility parameters for each component of the mixture.

In addition, we have defined our invention in terms of the calculated solubility

10   parameters of the monomers and solvents obtained using the group contribution method developed by Small, P. A., J. Appl. Chem., 3, 71 (1953) using Small's group contribution values listed in Table 2.2 on page VII/525 in the Polymer Handbook, 3rd Ed., J. Brandrup & E. H. Immergut, Eds. John Wiley, New York, (1989). We have chosen this method for defining our invention to avoid ambiguities which could result from using solubility

15   parameter values obtained with different experimental methods. In addition, Small's group contribution values will generate solubility parameters that are consistent with data derived from measurements of the enthalpy of vaporization, and therefore are completely consistent with the defining expression for the Hildebrand solubility parameter. Since it is not practical to measure the heat of vaporization for polymers, monomers are a

20   reasonable substitution.

For purposes of illustration, Table I lists Hildebrand solubility parameters for some common solvents used in an electrophotographic toner and the Hildebrand solubility parameters and glass transition temperatures (based on their high molecular weight homopolymers) for some common monomers used in synthesizing organosols.

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TABLE I

Hildebrand Solubility Parameters Solvent Values at 25°C		
Solvent Name	Kauri-Butanol Number by ASTM Method D1133-54T (ml)	Hildebrand Solubility Parameter $(MPa^{1/2})$
Norpar™ 15	18	13.99
Norpar™ 13	22	14.24
Norpar™ 12	23	14.30
Isopar™ V	25	14.42
Isopar™ G	28	14.60
Exxsol™ D80	28	14.60
Source: Calculated from equation #31 of Polymer Handbook, 3rd Ed., J. Brandrup E. H. Immergut, Eds. John Wiley, NY, p. VII/522 (1989).		

Monomer Values at 25°C		
Monomer Name	Hildebrand Solubility Parameter $(MPa^{1/2})$	Glass Transition Temperature (°C)*
3,3,5-Trimethyl Cyclohexyl Methacrylate	16.73	125
Isobornyl Methacrylate	16.90	110
Isobornyl Acrylate	16.01	94
n-Behenyl acrylate	16.74	< -55 (58 m.p.)**
n-Octadecyl Methacrylate	16.77	-100 (45 m.p.) **
n-Octadecyl Acrylate	16.82	-55
Lauryl Methacrylate	16.84	-65
Lauryl Acrylate	16.95	-30
2-Ethylhexyl Methacrylate	16.97	-10
2-Ethylhexyl Acrylate	17.03	-55
n-Hexyl Methacrylate	17.13	-5
t-Butyl Methacrylate	17.16	107
n-Butyl Methacrylate	17.22	20
n-Hexyl Acrylate	17.30	-60
n-Butyl Acrylate	17.45	-55
Ethyl Methacrylate	17.62	65
Ethyl Acrylate	18.04	-24
Methyl Methacrylate	18.17	105
Styrene	18.05	100
Calculated using Small's Group Contribution Method, Small, P.A. Journal of Applied Chemistry 3 p. 71 (1953). Using Group Contributions from Polymer Handbook, 3rd Ed., J. Brandrup E. H. Immergut, Eds., John Wiley, NY, p. VII/525 (1989). *Polymer Handbook, 3rd Ed., J. Brandrup E. H. Immergut, Eds., John Wiley, NY, pp. VII/209-277 (1989). The T_g listed is for the homopolymer of the respective monomer. ** m.p. refers to melting point for selected Polymerizable Crystallizable Compounds.		

The liquid carrier is a substantially nonaqueous solvent or solvent blend. In other

5   words, only a minor component (generally less than 25 weight percent) of the liquid

carrier comprises water. Preferably, the substantially nonaqueous liquid carrier comprises less than 20 weight percent water, more preferably less than 10 weight percent water, even more preferably less than 3 weight percent water, most preferably less than one weight percent water.

5   The carrier liquid may be selected from a wide variety of materials, or combination of materials, which are known in the art, but preferably has a Kauri-butanol number less than 30 ml. The liquid is preferably oleophilic, chemically stable under a variety of conditions, and electrically insulating. Electrically insulating refers to a dispersant liquid having a low dielectric constant and a high electrical resistivity.

10   Preferably, the liquid dispersant has a dielectric constant of less than 5; more preferably less than 3. Electrical resistivities of carrier liquids are typically greater than 10^9 Ohm-cm; more preferably greater than 10^{10} Ohm-cm. In addition, the liquid carrier desirably is chemically inert in most embodiments with respect to the ingredients used to formulate the toner particles.

15   Examples of suitable liquid carriers include aliphatic hydrocarbons (n-pentane, hexane, heptane and the like), cycloaliphatic hydrocarbons (cyclopentane, cyclohexane and the like), aromatic hydrocarbons (benzene, toluene, xylene and the like), halogenated hydrocarbon solvents (chlorinated alkanes, fluorinated alkanes, chlorofluorocarbons and the like) silicone oils and blends of these solvents. Preferred carrier liquids include

20   branched paraffinic solvent blends such as Isopar™ G, Isopar™ H, Isopar™ K, Isopar™ L, Isopar™ M and Isopar™ V (available from Exxon Corporation, NJ), and most preferred carriers are the aliphatic hydrocarbon solvent blends such as Norpar™ 12, Norpar™ 13 and Norpar™ 15 (available from Exxon Corporation, NJ).). Particularly preferred carrier liquids have a Hildebrand solubility parameter of from about 13 to about 15 MPa$^{1/2}$.

25   The liquid carrier of the toner compositions of the present invention is preferably the same liquid as used as the solvent for preparation of the amphipathic copolymer. Alternatively, the polymerization may be carried out in any appropriate solvent, and a solvent exchange may be carried out to provide the desired liquid carrier for the toner composition.

30   As used herein, the term "copolymer" encompasses both oligomeric and polymeric materials, and encompasses polymers incorporating two or more monomers.

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As used herein, the term "monomer" means a relatively low molecular weight material (i.e., generally having a molecular weight less than about 500 Daltons) having one or more polymerizable groups. "Oligomer" means a relatively intermediate sized molecule incorporating two or more monomers and generally having a molecular weight of from about 500 up to about 10,000 Daltons. "Polymer" means a relatively large material comprising a substructure formed two or more monomeric, oligomeric, and/or polymeric constituents and generally having a molecular weight greater than about 10,000 Daltons.

The term "macromer" or "macromonomer" refers to an oligomer or polymer having a terminal polymerizable moiety. "Polymerizable crystallizable compound" or "PCC" refers to compounds capable of undergoing polymerization to produce a copolymer wherein at least a portion of the copolymer is capable of undergoing reversible crystallization over a reproducible and well-defined temperature range (e.g. the copolymer exhibits a melting and freezing point as determined, for example, by differential scanning calorimetry). PCC's may include monomers, functional oligomers, functional pre-polymers, macromers or other compounds able to undergo polymerization to form a copolymer. The term "molecular weight" as used throughout this specification means weight average molecular weight unless expressly noted otherwise.

The weight average molecular weight of the amphipathic copolymer of the present invention may vary over a wide range, and may impact imaging performance. The polydispersity of the copolymer also may impact imaging and transfer performance of the resultant liquid toner material. Because of the difficulty of measuring molecular weight for an amphipathic copolymer, the particle size of the dispersed copolymer (organosol) may instead be correlated to imaging and transfer performance of the resultant liquid toner material. Generally, the volume mean particle diameter (D_v) of the dispersed graft copolymer particles, determined by laser diffraction particle size measurement, preferably should be in the range 0.1-100 microns, more preferably 0.5-50 microns, even more preferably 1.0-20 microns, and most preferably 2-10 microns.

In addition, a correlation exists between the molecular weight of the solvatable or soluble S portion of the graft copolymer, and the imaging and transfer performance of the resultant toner. Generally, the S portion of the copolymer has a weight average molecular weight in the range of 1000 to about 1,000,000 Daltons, preferably 5000 to

500,000 Daltons, more preferably 50,000 to 400,000 Daltons. It is also generally desirable to maintain the polydispersity (the ratio of the weight-average molecular weight to the number average molecular weight) of the S portion of the copolymer below 15, more preferably below 5, most preferably below 2.5. It is a distinct advantage of the present invention that copolymer particles with such lower polydispersity characteristics for the S portion are easily made in accordance with the practices described herein, particularly those embodiments in which the copolymer is formed in the liquid carrier in situ.

The relative amounts of S and D portions in a copolymer can impact the solvating and dispersibility characteristics of these portions. For instance, if too little of the S portion(s) are present, the copolymer may have too little stabilizing effect to sterically-stabilize the organosol with respect to aggregation as might be desired. If too little of the D portion(s) are present, the small amount of D material may be too soluble in the liquid carrier such that there may be insufficient driving force to form a distinct particulate, dispersed phase in the liquid carrier. The presence of both a solvated and dispersed phase helps the ingredients of particles self assemble in situ with exceptional uniformity among separate particles. Balancing these concerns, the preferred weight ratio of D material to S material is in the range of 1:1 to 20:1, more preferably 2:1 to 15:1, and most preferably 4:1 to 10:1.

Glass transition temperature, T_g, refers to the temperature at which a (co)polymer, or portion thereof, changes from a hard, glassy material to a rubbery, or viscous, material, corresponding to a dramatic increase in free volume as the (co)polymer is heated. The T_g can be calculated for a (co)polymer, or portion thereof, using known T_g values for the high molecular weight homopolymers (see, e.g., Table I herein) and the Fox equation expressed below:

$$1/ T_g = w_1/ T_{g1} + w_2/ T_{g2} + \ldots w_i/ T_{gi}$$

wherein each w_n is the weight fraction of monomer "n" and each T_{gn} is the absolute glass transition temperature (in degrees Kelvin) of the high molecular weight homopolymer of

monomer "n" as described in Wicks, A. W., F. N. Jones & S. P. Pappas, Organic
Coatings 1, John Wiley, NY, pp 54-55 (1992).

In the practice of the present invention, values of T_g for the D or S portion of the
copolymer were determined using the Fox equation above, although the T_g of the
copolymer as a whole may be determined experimentally using, e.g. differential scanning
calorimetry. The glass transition temperatures (T_g's) of the S and D portions may vary
over a wide range and may be independently selected to enhance manufacturability
and/or performance of the resulting liquid toner particles. The Tg's of the S and D
portions will depend to a large degree upon the type of monomers constituting such
portions. Consequently, to provide a copolymer material with higher Tg, one can select
one or more higher Tg monomers with the appropriate solubility characteristics for the
type of copolymer portion (D or S) in which the monomer(s) will be used. Conversely, to
provide a copolymer material with lower Tg, one can select one or more lower Tg
monomers with the appropriate solubility characteristics for the type of portion in which
the monomer(s) will be used.

As mentioned above, selection of glass transition temperature of the binder has an
impact on conditions in which film forming takes place, and also has impact on the final
properties of the image formed by the toner. In addition, the selection of the carrier
liquid also impacts the film forming and final product properties of the image formed by
the toner. Thus, a binder that has a high T_g may exhibit a lower effective T_g under certain
conditions by selection of a carrier liquid that strongly solvates that particular binder
composition. Likewise a binder having a lower T_g may not coalesce (i.e. form a film) if
the carrier liquid is selected so that the effective T_g is higher than theoretical under
conditions of use. Additionally, selection of various monomer components may alter the
observed behavior of the binder both on the photoreceptor during image formation and on
the final receptor layer due to chemical or steric interactions between components of the
binder. For example, as discussed in more detail below, a binder having a theoretically
lower T_g may not form a film under certain conditions at or above the theoretical T_g if it
contains crystalline moieties that have a high "activation" temperature for melting, but
yet may form an excellent film under appropriate processing conditions.

For copolymers useful in liquid toner applications, the copolymer T_g preferably should not be too low or else receptors printed with the toner may experience undue blocking. Conversely, the minimum fusing temperature required to soften or melt the toner particles sufficient for them to adhere to the final image receptor will increase as

5   the copolymer T_g increases. Consequently, it is preferred that the T_g of the copolymer be far enough above the expected maximum storage temperature of a printed receptor so as to avoid blocking issues, yet not so high as to require fusing temperatures approaching the temperatures at which the final image receptor may be damaged, e.g. approaching the autoignition temperature of paper used as the final image receptor. In this regard,

10   incorporation of a polymerizable crystallizable compound (PCC) in the copolymer will generally permit use of a lower copolymer T_g and therefore lower fusing temperatures without the risk of the image blocking at storage temperatures below the melting temperature of the PCC. Desirably, therefore, the copolymer has a T_g of 25°-100°C, more preferably 30°-80°C, and most preferably 40°-70°C.

15   For copolymers in which the D portion comprises a major portion of the copolymer, the T_g of the D portion will dominate the T_g of the copolymer as a whole. For such copolymers useful in liquid toner applications, it is preferred that the T_g of the D portion fall in the range of 30°-105°C, more preferably 40°-95°C, still more preferably 45°-85°C, most preferably 50° to 65°C. The S portion will generally exhibit a lower T_g

20   than the D portion, and a higher T_g D portion is therefore desirable to offset the T_g lowering effect of the S portion, which may be solvatable. In this regard, incorporation of a polymerizable crystallizable compound (PCC) in the D portion of the copolymer will generally permit use of a lower D portion T_g and therefore lower fusing temperatures without the risk of the image blocking at storage temperatures below the melting

25   temperature of the PCC. Formulation of particles that do not film form under Photoreceptor Image Formation conditions is facilitated by selection of D portion components such that the D material preferably has a T_g of at least about 55°C, and more preferably at least about 65°C.

        Blocking with respect to the S portion material is not as significant an issue

30   inasmuch as preferred copolymers comprise a majority of the D portion material having a relatively high T_g. Consequently, the T_g of the D portion material will dominate the

effective T_g of the copolymer as a whole. However, if the T_g of the S portion is too low, then the particles might tend to aggregate. On the other hand, if the T_g is too high, then the requisite fusing temperature may be too high. Balancing these concerns, the S portion material is preferably formulated to have a T_g of at least 0°C, preferably at least 20°C,

5   more preferably at least 40°C. In this regard, incorporation of a polymerizable crystallizable compound (PCC) in the S portion of the copolymer will generally permit use of a lower S portion T_g.

Preferred copolymers of the present invention may be formulated with one or more radiation curable monomers or combinations thereof that help the free radically

10   polymerizable compositions and/or resultant cured compositions to satisfy one or more desirable performance criteria. For example, in order to promote hardness and abrasion resistance, a formulator may incorporate one or more free radically polymerizable monomer(s) (hereinafter "high T_g component") whose presence causes the polymerized material, or a portion thereof, to have a higher glass transition temperature, T_g, as

15   compared to an otherwise identical material lacking such high T_g component. Preferred monomeric constituents of the high T_g component generally include monomers whose homopolymers have a T_g of at least about 50°C, preferably at least about 60°C, and more preferably at least about 75°C in the cured state.

The advantages of incorporating High T_g Monomer into the D material portions of

20   the copolymer are further described in assignee's co-pending U.S. Patent Application titled **ORGANOSOL INCLUDING HIGH T_g AMPHIPATHIC COPOLYMERIC BINDER AND LIQUID TONERS FOR ELECTROPHOTOGRAPHIC APPLICATIONS**, which is attorney docket number SAM0005/US, and filed on even date, in the names of Julie Y. Qian et al., said co-pending patent application being

25   incorporated herein by reference in its entirety.

An exemplary class of radiation curable monomers that tend to have relatively high T_g characteristics suitable for incorporation into the high T_g component generally comprises at least one radiation curable (meth)acrylate moiety and at least one nonaromatic, alicyclic and/or nonaromatic heterocyclic moiety. Isobornyl (meth)acrylate

30   is a specific example of one such monomer. A cured, homopolymer film formed from isobornyl acrylate, for instance, has a T_g of 110°C. The monomer itself has a molecular

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weight of 222 g/mole, exists as a clear liquid at room temperature, has a viscosity of 9 centipoise at 25°C, and has a surface tension of 31.7 dynes/cm at 25°C. Additionally, 1,6-Hexanediol di(meth)acrylate is another example of a monomer with high T_g characteristics.

5   Particularly preferred monomers for use in the D portion of the amphipathic copolymer include trimethyl cyclohexyl methacrylate; ethyl methacrylate; ethyl acrylate; isobornyl (meth)acrylate; 1,6-Hexanediol di(meth)acrylate and methyl methacrylate. Particularly preferred monomers for use in the S portion of the amphipathic copolymer include lauryl methacrylate, 2-hydroxyethyl methacrylate, dimethyl-m-isopropenyl

10   benzyl isocyanate, trimethyl cyclohexyl methacrylate, and ethyl hexyl methacrylate.

The amphipathic copolymer may optionally be provided with a Soluble High T_g Monomer having a T_g greater than about 55°C (more preferably greater than about 80°C). By "soluble" in the context of this aspect of the present invention is meant that the absolute difference in Hildebrand solubility parameters between the Soluble High T_g

15   Monomer and the liquid carrier is less than about 2.2 $MPa^{1/2}$.

The advantages of incorporating Soluble High T_g Monomer into the copolymer are further described in assignee's co-pending U.S. Patent Application titled **ORGANOSOL INCLUDING AMPHIPATHIC COPOLYMERIC BINDER MADE WITH SOLUBLE HIGH T_g MONOMER AND LIQUID TONERS FOR**

20   **ELECTROPHOTOGRAPHIC APPLICATIONS**, which is attorney docket number SAM0006/US and filed on even date, in the names of Julie Y. Qian et al., said co-pending patent application being incorporated herein by reference in its entirety.

Trimethyl cyclohexyl methacrylate (TCHMA) is one example of a high T_g monomer particularly useful in the practice of the present invention. TCHMA has a T_g of

25   125°C and tends to be solvatable or soluble in oleophilic solvents. Consequently, TCHMA is easily incorporated into S material. However, if used in limited amounts so as not to unduly impair the insolubility characteristics of D material, some TCHMA can also be incorporated into the D material.

As noted above, the Soluble High T_g soluble monomers are selected so that they

30   have a T_g of at least about 20°C, and wherein the absolute difference in Hildebrand solubility parameters between the Soluble High T_g Monomer and the liquid carrier is less

than about 3 $MPa^{1/2}$. Preferably the Soluble High T_g Monomer has a T_g at least about 40°C, more preferably at least about 60°C, and most preferably at least about 100°C. Most preferably, the absolute difference in Hildebrand solubility parameters between the Soluble High T_g Monomer and the liquid carrier is less than about 2.2 $MPa^{1/2}$.

5   Preferably, the Soluble High T_g Monomer is present at a concentration of between about 5 and 30% by weight of the amphipathic copolymer.

Trimethyl cyclohexyl methacrylate (TCHMA) is a particularly preferred example of a Soluble High T_g monomer useful in the practice of the present invention. TCHMA has a T_g of 125°C and tends to be soluble in oleophilic solvents. Consequently, TCHMA

10   is easily incorporated into S material. However, if used in limited amounts so as not to unduly impair the insolubility characteristics of D material, some TCHMA can also be incorporated into the D material.

A wide variety of one or more different monomeric, oligomeric and/or polymeric materials may be independently incorporated into the S and D portions, as desired.

15   Representative examples of suitable materials include free radically polymerized material (also referred to as vinyl copolymers or (meth) acrylic copolymers in some embodiments), polyurethanes, polyester, epoxy, polyamide, polyimide, polysiloxane, fluoropolymer, polysulfone, combinations of these, and the like. Preferred S and D portions are derived from free radically polymerizable material. In the practice of the

20   present invention, "free radically polymerizable " refers to monomers, oligomers, and/or polymers having functionality directly or indirectly pendant from a monomer, oligomer, or polymer backbone (as the case may be) that participate in polymerization reactions via a free radical mechanism. Representative examples of such functionality include (meth)acrylate groups, olefinic carbon-carbon double bonds, allyloxy groups, alpha-

25   methyl styrene groups, (meth)acrylamide groups, cyanate ester groups, vinyl ether groups, combinations of these, and the like. The term "(meth)acryl", as used herein, encompasses acryl and/or methacryl.

Free radically polymerizable monomers, oligomers, and/or polymers are advantageously used to form the copolymer in that so many different types are

30   commercially available and may be selected with a wide variety of desired characteristics that help provide one or more desired performance characteristics. Free radically

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polymerizable monomers, oligomers, and/or monomers suitable in the practice of the present invention may include one or more free radically polymerizable moieties.

Representative examples of monofunctional, free radically polymerizable monomers include styrene, alpha-methylstyrene, substituted styrene, vinyl esters, vinyl ethers, N-vinyl-2-pyrrolidone, (meth)acrylamide, vinyl naphthalene, alkylated vinyl naphthalenes, alkoxy vinyl naphthalenes, N-substituted (meth)acrylamide, octyl (meth)acrylate, nonylphenol ethoxylate (meth)acrylate, N-vinyl pyrrolidone, isononyl (meth)acrylate, isobornyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, beta-carboxyethyl (meth)acrylate, isobutyl (meth)acrylate, cycloaliphatic epoxide, alpha-epoxide, 2-hydroxyethyl (meth)acrylate, (meth)acrylonitrile, maleic anhydride, itaconic acid, isodecyl (meth)acrylate, lauryl (dodecyl) (meth)acrylate, stearyl (octadecyl) (meth)acrylate, behenyl (meth)acrylate, n-butyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, hexyl (meth)acrylate, (meth)acrylic acid, N-vinylcaprolactam, stearyl (meth)acrylate, hydroxy functional caprolactone ester (meth)acrylate, isooctyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxymethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxyisopropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyisobutyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, glycidyl (meth)acrylate vinyl acetate, combinations of these, and the like.

Nitrile functionality may be advantageously incorporated into the copolymer for a variety of reasons, including improved durability, enhanced compatibility with visual enhancement additive(s), e.g., colorant particles, and the like. In order to provide a copolymer having pendant nitrile groups, one or more nitrile functional monomers can be used. Representative examples of such monomers include (meth)acrylonitrile, β-cyanoethyl-(meth)acrylate, 2-cyanoethoxyethyl (meth)acrylate, p-cyanostyrene, p-(cyanomethyl)styrene, N-vinylpyrrolidinone, and the like.

Additional functionality may also be incorporated into the copolymer that is renders the copolymer crosslinkable after image development on the final receptor. The advantages of incorporating such crosslinkable functionalities into the copolymer are further described in assignee's co-pending U.S. Patent Application titled

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ORGANOSOL LIQUID TONER INCLUDING AMPHIPATHIC COPOLYMERIC BINDER HAVING CROSSLINKABLE FUNCTIONALITY, having serial number **60/437,881** and filed on **January 3, 2003** in the names of James A. Baker et al., said co-pending patent application being incorporated herein by reference in its entirety.

5   In certain preferred embodiments, polymerizable crystallizable compounds, e.g. crystalline monomer(s) are incorporated into the copolymer by chemical bonding to the copolymer. The term "crystalline monomer" refers to a monomer whose homopolymeric analog is capable of independently and reversibly crystallizing at or above room temperature (e.g., 22°C). The term "chemical bonding" refers to a covalent bond or other

10   chemical link between the polymerizable crystallizable compound and one or more of the other constituents of the copolymer. The advantages of incorporating PCC's into the copolymer are further described in assignee's co-pending U.S. Patent Application titled **ORGANOSOL LIQUID TONER INCLUDING AMPHIPATHIC COPOLYMERIC BINDER HAVING CRYSTALLINE COMPONENT,** having attorney docket number

15   SAM0004/US, and filed on even date in the names of Julie Y. Qian et al., said co-pending patent application being incorporated herein by reference in its entirety.

In these embodiments, the resulting toner particles can exhibit improved blocking resistance between printed receptors and reduced offset during fusing. If used, one or more of these crystalline monomers may be incorporated into the S and/or D material, but

20   preferably is incorporated into the D material. Suitable crystalline monomers include alkyl(meth)acrylates where the alkyl chain contains more than 13 carbon atoms (e.g. tetradecyl(meth)acrylate, pentadecyl(meth)acrylate, hexadecyl(meth)acrylate, heptadecyl(meth)acrylate, octadecyl(meth)acrylate, etc). Other suitable crystalline monomers whose homopolymers have melting points above 22°C include aryl acrylates

25   and methacrylates; high molecular weight alpha olefins; linear or branched long chain alkyl vinyl ethers or vinyl esters; long chain alkyl isocyanates; unsaturated long chain polyesters, polysiloxanes and polysilanes; polymerizable natural waxes with melting points above 22°C, polymerizable synthetic waxes with melting points above 22°C, and other similar type materials known to those skilled in the art. As described herein,

30   incorporation of crystalline monomers in the copolymer provides surprising benefits to the resulting liquid toner particles.

It will be understood by those skilled in the art that blocking resistance can be observed at temperatures above room temperature but below the crystallization temperature of the polymer portion incorporating the crystalline monomers or other polymerizable crystallizable compound. Improved blocking resistance is observed when

5   the crystalline monomer or PCC is a major component of the S material, preferably greater than 45%, more preferably greater than or equal to 75%, most preferably greater than or equal to 90% of the S material incorporated into the copolymer.

Many crystalline monomers tend to be soluble in oleophilic solvents commonly used as liquid carrier material(s) in an organosol. Thus, crystalline monomers are

10   relatively easily incorporated into S material without impacting desired solubility characteristics. However, if too much of such crystalline monomer were to be incorporated into D material, the resultant D material may tend to be too soluble in the organosol. Yet, so long as the amount of soluble, crystalline monomer in the D material is limited, some amount of crystalline monomer may be advantageously incorporated into

15   the D material without unduly impacting the desired insolubility characteristics. Thus, when present in the D material, the crystalline monomer is preferably provided in an amount of up to about 30%, more preferably up to about 20%, most preferably up to about 5% to 10% of the total D material incorporated into the copolymer.

When crystalline monomers or PCC's are incorporated chemically into the S

20   material, suitable co-polymerizable compounds to be used in combination with the PCC include monomers (including other PCC's) such as 2-ethylhexyl acrylate, 2-ethylhexyl (methacrylate), lauryl acrylate, lauryl methacrylate, octadecyl acrylate, octadecyl(methacrylate), isobornyl acrylate, isobornyl (methacrylate), hydroxy(ethylmethacrylate), and other acrylates and methacrylates.

25   Suitable free radically reactive oligomer and/or polymeric materials for use in the present invention include, but are not limited to, (meth)acrylated urethanes (i.e., urethane (meth)acrylates), (meth)acrylated epoxies (i.e., epoxy (meth)acrylates), (meth)acrylated polyesters (i.e., polyester (meth)acrylates), (meth)acrylated (meth)acrylics, (meth)acrylated silicones, (meth)acrylated polyethers (i.e., polyether (meth)acrylates),

30   vinyl (meth)acrylates, and (meth)acrylated oils.

Gelation is induced as a result of weak attractive forces arising from hydrogen bonding association between one or more covalently bonded hydrogen atoms and another more electronegative atom in a hydrogen bonding polymerizable compound, as described in Allan F. M. Barton, Handbook of Solubility and Other Cohesion Parameters (CRC

5   Press: Boca Raton, FL, 1991 pp. 72-75). Hydrogen-bonding polymerizable compounds include those in which a single compound comprises both a covalently bound hydrogen atom capable of acting as a Bronsted acid proton donor, and an electronegative atom capable of donating an electron pair to a proton, thereby forming the hydrogen bond. For convenience, we will refer to such compounds as self-associating, hydrogen-bonding,

10   polymerizable compounds. Alternatively, hydrogen-bonding, polymerizable compounds include those in which a single compound comprises either a covalently bound hydrogen atom capable of acting as a Bronsted acid and donating a proton, or an electronegative atom capable of donating an electron pair to a proton (also referred to herein as a hydrogen bond acceptor). For convenience, we will refer to such compounds as

15   conjunctively associating, hydrogen-bonding, polymerizable compounds. Conjunctively associating, hydrogen-bonding, polymerizable compounds may be further identified as either proton donors or electron pair donors. In order to form intermolecular hydrogen bonds, it is necessary to incorporate both a proton donor and an electron pair donor conjunctively associating, polymerizable compound in the composition as a donor pair.

20   In one embodiment, gelation is induced by incorporating a single self-associating, hydrogen-bonding, polymerizable compound in the amphipathic copolymer organosol. The hydrogen-bonding polymerizable compound may be incorporated in the organosol D material portion, in the organosol S material portion, or in both the organosol D material portion and S material portion. Preferably, the hydrogen-bonding

25   polymerizable compound is incorporated in the organosol S material portion.

In another embodiment, two or more different conjunctively associating, hydrogen-bonding, polymerizable compounds are incorporated in the organosol D material portion, in the organosol S material portion, or in both the organosol D material portion and S material portion. Preferably, the hydrogen-bonding polymerizable

30   compounds are both incorporated in the organosol S material portion.

In a third embodiment, two distinct organosols are prepared. One organosol comprises one or more proton donor, conjunctively associating, hydrogen-bonding polymerizable compounds in the organosol D material portion, in the organosol S material portion, or in both the organosol D material portion and S material portion.

5   The other organosol comprises one or more electron pair donor, conjunctively associating, hydrogen-bonding polymerizable compounds in the organosol D material portion, in the organosol S material portion, or in both the organosol D material portion and S material portion. This approach has the advantage that gelation will not occur until the two organosols are blended together, or until links comprising the two distinct

10   organosols are blended together. This permits easy handling of two self-stable organosols until the organosols are combined with a colorant, to make a gel ink.

In either of the above embodiments, the composition may optionally be provided with an additional polyfunctional bridging compound having at least two of hydrogen bond donor or acceptor functionalities to assist in gel formation.

15   In a third embodiment, an amphipathic copolymer organosol is prepared having only hydrogen bond donor functional polymerizable compound in the D material portion and/or S material portion. A polyfunctional bridging compound having at least two hydrogen bond acceptor functionalities on the compound is provided in the composition in an amount effective to form a gel.

20   In a fourth embodiment, an amphipathic copolymer organosol is prepared having only hydrogen bond acceptor functional polymerizable compound in the D material portion and/or S material portion. A polyfunctional bridging compound having at least two hydrogen bond donor functionalities on the compound is provided in the composition in an amount effective to form a gel.

25   Suitable self-associating, hydrogen-bonding, polymerizable compounds include acrylic acid, methacrylic acid, 2-acrylamido-2-methyl propane sulfonic acid, allyl alcohol, allyl amine, allyl ethylamine, allyl hydroxyethyl ether, p-amino styrene, t-butylamino methacrylate, cinnamyl alcohol, crotonic acid, diallyl amine, 2,3-dihydroxy propyl acrylate, dipentaerythritol monohydroxypentaacrylate, 4-hydroxybutyl acrylate, 4-

30   hydroxybutyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl methacrylate, 4-hydroxy styrene, itaconic

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acid, maleic acid, methallylamine, pentaerythritol tetraacrylate, pentaerythritol triacrylate, polypropylene glycol monomethyl methacrylate, tris (2-hydroxyethyl)isocyanurate triacrylate, vinyl benzene alcohol, and 4-vinyl benzoic acid.

Suitable conjunctively associating, hydrogen-bonding, polymerizable compounds that can act as proton donors include all self-associating, hydrogen-bonding, polymerizable compounds.

Suitable conjunctively associating, hydrogen-bonding, polymerizable compounds that can act as electron pair donors include all self-associating, hydrogen-bonding, polymerizable compounds, as well as allyl mercaptan, allyl dimethylamine, N-allyl piperidine, 1,3-butanediol diacrylate, 1,4-butanediol diacrylate, 2-butoxyethyl acrylate, 2-butoxyethyl methacrylate, bis diallylamino methane, N,N-diallylmelamine, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 2-diisopropylamino ethyl methacrylate, 2-dimethylaminoethyl methacrylate, 2-dimethylamino methyl styrene, 3-dimethylamino neopentyl acrylate, acrylamide, diacetone acrylamide, dimethylaminopropyl acrylamide, 2,3-epoxypropyl methacrylate (glycidyl methacrylate), 2-(2-ethoxyethoxy) ethyl acrylate, 2-(2-ethoxyethoxy) ethyl methacrylate, ethoxylated Bisphenol A diacrylate, ethoxylated trimethylol triacrylate, ethoxylated trimethylolpropane triacrylate, ethylene glycol dimethacrylate, glyceryl propoxy triacrylate, 1,6 hexanediol diacrylate, glycidyl methacrylate, 1,6 hexanediol diacrylate, 1,6 hexanediol dimethacrylate, isobutyl vinyl ether, 2-methoxyethyl acrylate, neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, pentaerythritol tetraacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, propoxylated neopentyl glycol diacrylate, propoxylated neopentyl glycol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tripropylene glycol diacrylate, tripropylene glycol dimethacrylate, vinyl benzene dimethylamine, 2-vinyl pyridine, 4-vinyl pyridine, and N-vinyl-2-pyrrolidone.

The extent of gelation of the hydrogen-bonded gel organosol may be controlled by manipulating the concentration of hydrogen-bonding polymerizable compound

incorporated into the amphipathic copolymer. Generally, a higher concentration of hydrogen-bonding polymerizable compound leads to a higher apparent hydrogen-bond density and therefore a stronger gel. However, too high a concentration of hydrogen-bonding polymerizable monomer will cause the amphipathic copolymer to solidify into a

5   solid-like polymer matrix that is not suitable for incorporation into a crosslinked gel organosol.

The preferable amount of hydrogen-bonding polymerizable compound comprising the amphipathic copolymer will depend upon the desired gel strength, as well as whether the hydrogen-bonding polymerizable compound is incorporated in the graft

10   copolymer S material portion only, the amphipathic copolymer D material portion only, or both the S material portion and the D material portion. When the hydrogen-bonding polymerizable compound is incorporated only in the S material portion, it is preferably incorporated in the range of 0.1-17% w/w, more preferably 1-12% w/w, most preferably 3-6% w/w based on the S material portion weight. When the hydrogen-bonding

15   polymerizable compound is incorporated only in the D material portion, it is preferably incorporated in the rage of 0.1-20% w/w, more preferably 1-12% w/w, most preferably 3-7% w/w based on the D material portion weight. When the hydrogen-bonding polymerizable compound is incorporated both in the S material portion and the D material portion, it is preferably incorporated in the range of 0.1-12% w/w, more

20   preferably 1-8% w/w, most preferably 3-5% w/w based on the total amphipathic copolymer weight. The preferred concentration range of hydrogen-bonding polymerizable compounds will vary somewhat depending on the strength of the specific hydrogen bonds formed and whether the hydrogen-bonding polymerizable compound is self-associating or conjunctively associating.

25   Copolymers of the present invention can be prepared by free-radical polymerization methods known in the art, including but not limited to bulk, solution, and dispersion polymerization methods. The resultant copolymers may have a variety of structures including linear, branched, three dimensionally networked, graft-structured, combinations thereof, and the like. A preferred embodiment is a graft copolymer

30   comprising one or more oligomeric and/or polymeric arms attached to an oligomeric or

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polymeric backbone. In graft copolymer embodiments, the S portion or D portion materials, as the case may be, may be incorporated into the arms and/or the backbone.

Any number of reactions known to those skilled in the art may be used to prepare a free radically polymerized copolymer having a graft structure. Common grafting methods include random grafting of polyfunctional free radicals; copolymerization of monomers with macromonomers; ring-opening polymerizations of cyclic ethers, esters, amides or acetals; epoxidations; reactions of hydroxyl or amino chain transfer agents with terminally-unsaturated end groups; esterification reactions (i.e., glycidyl methacrylate undergoes tertiary-amine catalyzed esterification with methacrylic acid); and condensation polymerization.

Representative methods of forming graft copolymers are described in U.S. Pat. Nos. 6,255,363; 6,136,490; and 5,384,226; and Japanese Published Patent Document No. 05-119529, incorporated herein by reference. Representative examples of grafting methods are also described in sections 3.7 and 3.8 of Dispersion Polymerization in Organic Media, K.E.J. Barrett, ed., (John Wiley; New York, 1975) pp. 79-106, also incorporated herein by reference.

Representative examples of grafting methods also may use an anchoring group. The function of the anchoring group is to provide a covalently bonded link between the core part of the copolymer (the D material) and the soluble shell component (the S material). Suitable monomers containing anchoring groups include: adducts of alkenylazlactone comonomers with an unsaturated nucleophile containing hydroxy, amino, or mercaptan groups, such as 2-hydroxyethylmethacrylate, 3-hydroxypropylmethacrylate, 2-hydroxyethylacrylate, pentaerythritol triacrylate, 4-hydroxybutylvinylether, 9-octadecen-1-ol, cinnamyl alcohol, allyl mercaptan, methallylamine; and azlactones, such as 2-alkenyl-4,4-dialkylazlactone.

The preferred methodology described above accomplishes grafting via attaching an ethylenically-unsaturated isocyanate (e.g. dimethyl-m-isopropenyl benzylisocyanate, TMI, available from CYTEC Industries, West Paterson, NJ; or isocyanatoethyl methacrylate, IEM, available from Aldrich Chemical Company, Milwaukee, WI) or an epoxy functionality to hydroxyl groups or amine groups in order to provide free radically reactive anchoring groups.

A preferred method of forming a graft copolymer of the present invention involves three reaction steps that are carried out in a suitable substantially nonaqueous liquid carrier in which resultant S material is soluble while D material is dispersed or insoluble.

5 In a first preferred step, a hydroxyl functional, free radically polymerized oligomer or polymer is formed from one or more monomers, wherein at least one of the monomers has pendant hydroxyl functionality. Preferably, the hydroxyl functional monomer constitutes about 1 to about 30, preferably about 2 to about 10 percent, most preferably 3 to about 5 percent by weight of the monomers used to form the oligomer or

10 polymer of this first step. This first step is preferably carried out via solution polymerization in a substantially nonaqueous solvent in which the monomers and the resultant polymer are soluble. For instance, using the Hildebrand solubility data in Table 1, monomers such as octadecyl methacrylate, octadecyl acrylate, lauryl acrylate, and lauryl methacrylate are suitable for this first reaction step when using an oleophilic

15 solvent such as heptane or the like.

In a second reaction step, all or a portion of the hydroxyl groups of the soluble polymer are catalytically reacted with an ethylenically unsaturated aliphatic isocyanate (e.g. meta-isopropenyldimethylbenzyl isocyanate commonly known as TMI or isocyanatoethyl methacrylate, commonly known as IEM) to form pendant free radically

20 polymerizable functionality which is attached to the oligomer or polymer via a polyurethane linkage. This reaction can be carried out in the same solvent, and hence the same reaction vessel, as the first step. The resultant double-bond functionalized polymer generally remains soluble in the reaction solvent and constitutes the S portion material of the resultant copolymer, which ultimately will constitute at least a portion of the

25 solvatable portion of the resultant triboelectrically charged particles.

The resultant free radically reactive functionality provides grafting sites for attaching D material and optionally additional S material to the polymer. In a third step, these grafting site(s) are used to covalently graft such material to the polymer via reaction with one or more free radically reactive monomers, oligomers, and or polymers that are

30 initially soluble in the solvent, but then become insoluble as the molecular weight of the graft copolymer. For instance, using the Hildebrand solubility parameters in Table 1,

monomers such as e.g. methyl (meth)acrylate, ethyl (meth)acrylate, t-butyl methacrylate and styrene are suitable for this third reaction step when using an oleophilic solvent such as heptane or the like.

The product of the third reaction step is generally an organosol comprising the resultant copolymer dispersed in the reaction solvent, which constitutes a substantially nonaqueous liquid carrier for the organosol. At this stage, it is believed that the copolymer tends to exist in the liquid carrier as discrete, monodisperse particles having dispersed (e.g., substantially insoluble, phase separated) portion(s) and solvated (e.g., substantially soluble) portion(s). As such, the solvated portion(s) help to sterically-stabilize the dispersion of the particles in the liquid carrier. It can be appreciated that the copolymer is thus advantageously formed in the liquid carrier in situ.

Before further processing, the copolymer particles may remain in the reaction solvent. Alternatively, the particles may be transferred in any suitable way into fresh solvent that is the same or different so long as the copolymer has solvated and dispersed phases in the fresh solvent. In either case, the resulting organosol is then converted into toner particles by mixing the organosol with at least one visual enhancement additive. Optionally, one or more other desired ingredients also can be mixed into the organosol before and/or after combination with the visual enhancement particles. During such combination, it is believed that ingredients comprising the visual enhancement additive and the copolymer will tend to self-assemble into composite particles having a structure wherein the dispersed phase portions generally tend to associate with the visual enhancement additive particles (for example, by physically and/or chemically interacting with the surface of the particles), while the solvated phase portions help promote dispersion in the carrier.

In addition to the visual enhancement additive, other additives optionally can be formulated into the liquid toner composition. A particularly preferred additive comprises at least one charge control agent (CCA, charge control additive or charge director). The charge control agent, also known as a charge director, can be included as a separate ingredient and/or included as one or more functional moiety(ies) of the S and/or D material incorporated into the amphipathic copolymer. The charge control agent acts to enhance the chargeability and/or impart a charge to the toner particles. Toner particles

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can obtain either positive or negative charge depending upon the combination of particle material and charge control agent.

The charge control agent can be incorporated into the toner particles using a variety of methods, such as copolymerizing a suitable monomer with the other monomers used to form the copolymer, chemically reacting the charge control agent with the toner particle, chemically or physically adsorbing the charge control agent onto the toner particle (resin or pigment), or chelating the charge control agent to a functional group incorporated into the toner particle. One preferred method is via a functional group built into the S material of the copolymer.

The charge control agent acts to impart an electrical charge of selected polarity onto the toner particles. Any number of charge control agents described in the art can be used. For example, the charge control agent can be provided it the form of metal salts consisting of polyvalent metal ions and organic anions as the counterion. Suitable metal ions include, but are not limited to, Ba(II), Ca(II), Mn(II), Zn(II), Zr(IV), Cu(II), Al(III), Cr(III), Fe(II), Fe(III), Sb(III), Bi(III), Co(II), La(III), Pb(II), Mg(II), Mo(III), Ni(II), Ag(I), Sr(II), Sn(IV), V(V), Y(III), and Ti(IV). Suitable organic anions include carboxylates or sulfonates derived from aliphatic or aromatic carboxylic or sulfonic acids, preferably aliphatic fatty acids such as stearic acid, behenic acid, neodecanoic acid, diisopropylsalicylic acid, octanoic acid, abietic acid, naphthenic acid, lauric acid, tallic acid, and the like.

Preferred negative charge control agents are lecithin and basic barium petronate. Preferred positive charge control agents include metallic carboxylates (soaps), for example, as described in U.S. Pat. No. 3,411,936 (incorporated herein by reference). A particularly preferred positive charge control agent is zirconium tetraoctoate (available as Zirconium HEX-CEM from OMG Chemical Company, Cleveland, OH).

The preferred charge control agent levels for a given toner formulation will depend upon a number of factors, including the composition of the S portion and the organosol, the molecular weight of the organosol, the particle size of the organosol, the D:S ratio of the polymeric binder, the pigment used in making the toner composition, and the ratio of organosol to pigment. In addition, preferred charge control agent levels will depend upon the nature of the electrophotographic imaging process. The level of charge

control agent can be adjusted based upon the parameters listed herein, as known in the art. The amount of the charge control agent, based on 100 parts by weight of the toner solids, is generally in the range of 0.01 to 10 parts by weight, preferably 0.1 to 5 parts by weight.

5   The conductivity of a liquid toner composition can be used to describe the effectiveness of the toner in developing electrophotographic images. The liquid toners of the present invention are particularly suited for high solids discharge area development, e.g 5-25%, and more preferably 8-15 %. At these concentration ranges, the conductivity is preferably from about 1×10^{-11} mho/cm to about 3×10^{-10} mho/cm, and more

10   preferably from about 5×10^{-11} mho/cm to about 2.5×10^{-10} mho/cm. High conductivities generally indicate inefficient association of the charges on the toner particles and is seen in the low relationship between current density and toner deposited during development. Low conductivities indicate little or no charging of the toner particles and lead to very low development rates. The use of charge control agents matched to adsorption sites on

15   the toner particles is a common practice to ensure sufficient charge associates with each toner particle.

Other additives may also be added to the formulation in accordance with conventional practices. These include one or more of UV stabilizers, mold inhibitors, bactericides, fungicides, antistatic agents, gloss modifying agents, other polymer or

20   oligomer material, antioxidants, and the like.

The particle size of the resultant charged toner particles can impact the imaging, fusing, resolution, and transfer characteristics of the toner composition incorporating such particles. Preferably, the volume mean particle diameter (determined with laser diffraction) of the toner particles is in the range of about 0.05 to about 50.0 microns,

25   more preferably in the range of about 1.5 to about 10 microns, most preferably in the range of about 3 to about 5 microns.

The gel organosols of the present invention have been used to fabricate liquid electrophotographic toners that exhibit excellent imaging characteristics in liquid immersion development. For example, the gel organosol liquid toners exhibit low bulk

30   conductivity, low free phase conductivity, low charge/mass and high mobility, all desirable characteristics for producing high resolution, background free images with high

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optical density. In particular, the low bulk conductivity, low free phase conductivity and low charge/mass of the toners allow them to achieve high developed optical density over a wide range of solids concentrations, thus improving their extended printing performance relative to conventional toners.

5   Color liquid toners made according to this invention on development form substantially transparent films which transmit incident light at selected wavelengths (preferably >700 nm, more preferably >780 nm), consequently allowing the photoconductor layer to discharge, while non-coalescent particles scatter a portion of the incident light. Non-coalesced toner particles therefore result in the decreasing of the

10   sensitivity of the photoconductor to subsequent exposures and consequently there is interference with the overprinted image. This also permits latent image generation by Infrared laser scanning devices.

        While the electrostatic charge of either the toner particles or photoreceptive element may be either positive or negative, electrophotography as employed in the

15   present invention is preferably carried out by dissipating charge on a positively charged photoreceptive element. A positively-charged toner is then applied to the regions in which the positive charge was dissipated using a liquid toner development technique.

        The substrate for receiving the image from the photoreceptive element can be any commonly used receptor material, such as paper, coated paper, polymeric films and

20   primed or coated polymeric films. Polymeric films include polyesters and coated polyesters, polyolefins such as polyethylene or polypropylene, plasticized and compounded polyvinyl chloride (PVC), acrylics, polyurethanes, polyethylene/acrylic acid copolymer, and polyvinyl butyrals. The polymer film may be coated or primed, e.g. to promote toner adhesion.

25   In electrophotographic processes, the toner composition preferably is provided at a solids content of about 1-30%, more preferably 3-25%, and most preferably 5-20%. In electrostatic processes, the toner composition preferably is provided at a solids content of 3-15%.

        In a particularly preferred aspect of the present invention, toner compositions are

30   provided having a toner solids content of from about 20 to about 40%. These compositions are particularly suited for electrostatic imaging transfer processes wherein

the image is transferred from a photoconductive surface to another surface by a system comprising electrostatic forces to assist in the transfer of the image, without film formation prior to or during the image transfer step. Such systems are described, for example, in US Patent Application Nos. 2002/0110390 and 2003/0044202, the

5   disclosures of which are incorporated herein by reference.

These and other aspects of the present invention are demonstrated in the illustrative examples that follow.

EXAMPLES

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Test Methods and Apparatus

In the following examples, percent solids of the copolymer solutions and the organosol and ink dispersions were determined gravimetrically using the Halogen Lamp Drying Method using a halogen lamp drying oven attachment to a precision analytical

15   balance (Mettler Instruments, Inc., Highstown, N.J.). Approximately two grams of sample were used in each determination of percent solids using this sample dry down method.

In the practice of the invention, molecular weight is normally expressed in terms of the weight average molecular weight, while molecular weight polydispersity is given

20   by the ratio of the weight average molecular weight to the number average molecular weight. Molecular weight parameters were determined with gel permeation chromatography (GPC) using tetrahydrofuran as the carrier solvent. Absolute weight average molecular weight were determined using a Dawn DSP-F light scattering detector (Wyatt Technology Corp., Santa Barbara, Calif.), while polydispersity was evaluated by

25   ratioing the measured weight average molecular weight to a value of number average molecular weight determined with an Optilab 903 differential refractometer detector (Wyatt Technology Corp., Santa Barbara, Calif.).

Organosol and toner particle size distributions were determined by the Laser Diffraction Laser Diffraction Light Scattering Method using a Horiba LA-900 laser

30   diffraction particle size analyzer (Horiba Instruments, Inc., Irvine, Calif.). Samples are diluted approximately 1/500 by volume and sonicated for one minute at 150 watts and 20

kHz prior to measurement. Particle size was expressed as both a number mean diameter (D_n) and a volume mean diameter (D_v) and in order to provide an indication of both the fundamental (primary) particle size and the presence of aggregates or agglomerates.

The liquid toner conductivity (bulk conductivity, k_b) was determined at
5   approximately 18 Hz using a Scientifica Model 627 conductivity meter (Scientifica Instruments, Inc., Princeton, N.J.). In addition, the free (liquid dispersant) phase conductivity (k_f) in the absence of toner particles was also determined. Toner particles were removed from the liquid medium by centrifugation at 5°C for 1-2 hours at 6,000 rpm (6,110 relative centrifugal force) in a Jouan MR1822 centrifuge (Winchester, VA).
10   The supernatant liquid was then carefully decanted, and the conductivity of this liquid was measured using a Scientifica Model 627 conductance meter. The percentage of free phase conductivity relative to the bulk toner conductivity was then determined as 100% (k_f/k_b).

Toner particle electrophoretic mobility (dynamic mobility) was measured using a
15   Matec MBS-8000 Electrokinetic Sonic Amplitude Analyzer (Matec Applied Sciences, Inc., Hopkinton, MA). Unlike electrokinetic measurements based upon microelectro-phoresis, the MBS-8000 instrument has the advantage of requiring no dilution of the toner sample in order to obtain the mobility value. Thus, it is possible to measure toner particle dynamic mobility at solids concentrations actually preferred in printing. The
20   MBS-8000 measures the response of charged particles to high frequency (1.2 MHz) alternating (AC) electric fields. In a high frequency AC electric field, the relative motion between charged toner particles and the surrounding dispersion medium (including counter-ions) generates an ultrasonic wave at the same frequency of the applied electric field. The amplitude of this ultrasonic wave at 1.2 MHz can be measured using a
25   piezoelectric quartz transducer; this electrokinetic sonic amplitude (ESA) is directly proportional to the low field AC electrophoretic mobility of the particles. The particle zeta potential can then be computed by the instrument from the measured dynamic mobility and the known toner particle size, liquid dispersant viscosity, and liquid dielectric constant.

30   The charge per mass measurement (Q/M) was measured using an apparatus that consists of a conductive metal plate, a glass plate coated with Indium Tin Oxide (ITO), a

high voltage power supply, an electrometer, and a personal computer (PC) for data acquisition. A 1% solution of ink was placed between the conductive plate and the ITO coated glass plate. An electrical potential of known polarity and magnitude was applied between the ITO coated glass plate and the metal plate, generating a current flow

5   between the plates and through wires connected to the high voltage power supply. The electrical current was measured 100 times a second for 20 seconds and recorded using the PC. The applied potential causes the charged toner particles to migrate towards the plate (electrode) having opposite polarity to that of the charged toner particles. By controlling the polarity of the voltage applied to the ITO coated glass plate, the toner particles may

10   be made to migrate to that plate.

The ITO coated glass plate was removed from the apparatus and placed in an oven for approximately 30 minutes at 50°C to dry the plated ink completely. After drying, the ITO coated glass plate containing the dried ink film was weighed. The ink was then removed from the ITO coated glass plate using a cloth wipe impregnated with

15 .   Norpar™ 12, and the clean ITO glass plate was weighed again. The difference in mass between the dry ink coated glass plate and the clean glass plate is taken as the mass of ink particles (m) deposited during the 20 second plating time. The electrical current values were used to obtain the total charge carried by the toner particles (Q) over the 20 seconds of plating time by integrating the area under a plot of current vs. time using a curve-

20   fitting program (e.g. TableCurve 2D from Systat Software Inc.). The charge per mass (Q/m) was then determined by dividing the total charge carried by the toner particles by the dry plated ink mass.

In the following examples, toner was printed onto final image receptors using the following methodology (referred to in the Examples as the Liquid Electrophotographic

25   Printing Method):

A light sensitive temporary image receptor (organic photoreceptor or "OPC") was charged with a uniform positive charge of approximately 850 volts. The positively charged surface of the OPC was image-wise irradiated with a scanning infrared laser module in order to reduce the charge wherever the laser struck the surface. Typical

30   charge-reduced values were between 50 volts and 100 volts.

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A developer apparatus was then utilized to apply the toner particles to the OPC surface. The developer apparatus included the following elements: a conductive rubber developer roll in contact with the OPC, liquid toner, a conductive deposition roll, an insulative foam cleaning roll in contact with developer roll surface, and a conductive

5   skiving blade (skive) in contact with the developer roll. The contact area between the developer roll and the OPC is referred to as the "developing nip." The developer roll and conductive deposition roll were both partially suspended in the liquid toner. The developer roll delivered liquid toner to the OPC surface, while the conductive deposition roll was positioned with its roll axis parallel to the developer roll axis and its surface

10   arranged to be approximately 150 microns from the surface of the developer roll, thereby forming a deposition gap.

    During development, toner was initially transferred to the developer roll surface by applying a voltage of approximately 500 volts to the conductive developer roll and applying a voltage of 600 volts to the deposition roll. This created a 100-volt potential

15   between the developer roll and the deposition roll so that in the deposition gap, toner particles (which were positively charged) migrated to the surface of the developer roll and remained there as the developer roll surface exited from the liquid toner into the air.

    The conductive metal skive was biased to at least 600 volts (or more) and skived liquid toner from the surface of the developer roll without scraping off the toner layer that

20   was deposited in the deposition gap. The developer roll surface at this stage contained a uniformly thick layer of toner at approximately 25% solids. As this toner layer passed through the developing nip, toner was transferred from the developer roll surface to the OPC surface in all the discharged areas of the OPC (the charge image), since the toner particles were positively charged. At the exit of the developing nip, the OPC contained a

25   toner image and the developer roll contained a negative of that toner image which was subsequently cleaned from the developer roll surface by encountering the rotating foam cleaning roll.

    The developed latent image (toned image) on the photoreceptor was subsequently transferred to the final image receptor without film formation of the toner on the OPC.

30   Transfer was effected either directly to the final image receptor, or indirectly using an electrostatically-assisted offset transfer to an Intermediate Transfer Belt (ITB), with

subsequent electrostatically-assisted offset transfer to the final image receptor. Smooth, clay coated papers were preferred final image receptors for direct transfer of a non-film formed toner from the photoreceptor, while plain, uncoated 20 pound bond paper was a preferred final image receptor for offset transfer using an electrostatic assist.

5   Electrostatically-assisted transfer of non film-formed toner was most effective when the transfer potential (potential difference between the toner on the OPC and the paper back-up roller for direct transfer; or potential difference between the toner on the OPC and the ITB for offset transfer) was maintained in the range of 200-1000 V or 800-2000 V, respectively.

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Materials

The following abbreviations are used in the examples:

LMA: lauryl methacrylate

TCHMA: trimethyl cyclohexyl methacrylate

15   BHA: behenyl acrylate

ODA: octadecyl acrylate

EA: ethyl acrylate

EMA: ethyl methacrylate

EHMA: 2-ethylhexyl methacrylate

20   HEMA: 2-hydroxyethyl methacrylate

MAA: methacrylic acid

AAM: acrylamide

DAAM: diacetone acrylamide

GMA: glycidyl methacrylate

25   TMI: dimethyl-m-isopropenyl benzyl isocyanate

V-601: initiator, dimethyl 2, 2'-azobisisobutyrate

DBTDL: catalyst, dibutyl tin dilaurate

Nomenclature

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In the following examples, the compositional details of each copolymer will be summarized by ratioing the weight percentages of monomers used to create the

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copolymer. The grafting site composition is expressed as a weight percentage of the monomers comprising the copolymer or copolymer precursor, as the case may be. For example, a graft stabilizer (precursor to the S portion of the copolymer) is designated TCHMA/HEMA-TMI (97/3-4.7) is made by copolymerizing, on a relative basis, 97 parts

5   by weight TCHMA and 3 parts by weight HEMA, and this hydroxy functional polymer was reacted with 4.7 parts by weight of TMI.

Examples 1-13: Preparation of Copolymer S materials, also referred to herein as "graft stabilizers"

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Example 1

A 32 ounce (0.96 liter), narrow-mouthed glass bottle was charged with 475 g of Norpar™ 12, 158 g of LMA, 5.0 g of 98% HEMA and 2.44 g of V-601. The bottle was purged for 1 minute with dry nitrogen at a rate of approximately 1.5 liters/minute, and

15   then sealed with a screw cap fitted with a Teflon liner. The cap was secured in place using electrical tape. The sealed bottle was then inserted into a metal cage assembly and installed on the agitator assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-Ometer was operated at its fixed agitation speed of 42 RPM with a water bath temperature of 70° C. The mixture was allowed to react for

20   approximately 16-18 hours, at which time the conversion of monomer to polymer was quantitative. The mixture was heated to 90° C for 1 hour to destroy any residual V-601, and then was cooled to room temperature.

The bottle was then opened and 2.5 g of 95% DBTDL and 7.6 g of TMI were added to cooled mixture. The bottle was sealed with a screw cap fitted with Teflon liner.

25   The cap was secured in place using electrical tape. The sealed bottle was then inserted into a metal cage assembly and installed on the agitator assembly of the Atlas Launder-Ometer. The Launder-Ometer was operated at its fixed agitation speed of 42 RPM with a water bath temperature of 70° C. The mixture was allowed to react for approximate 4-6 hours, at which time the conversion of monomer to polymer was quantitative. The cooled

30   mixture was a viscous, clear solution, containing no visible insoluble mater.

The percent solids of the liquid mixture was determined to be 24.72% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular

weight was made using the GPC method described above; the copolymer had a M_w of 131,600 Da and M_w/M_n of 2.3 based upon two independent measurements. The product is a copolymer of LMA and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA-TMI (97/3-4.7% w/w) and is suitable for making a non-gel organosol.

Example 2

A 5000 ml 3-neck round flask equipped with a condenser, a thermocouple connected to a digital temperature controller, a nitrogen inlet tube connected to a source of dry nitrogen and a magnetic stirrer, was charged with a mixture of 2556 g of Norpar™ 12, 823 g of LMA, 53.6 g of 98% HEMA and 13.13 g of V-601. While stirring the mixture, the reaction flask was purged with dry nitrogen for 30 minutes at flow rate of approximately 2 liters/minute. A hollow glass stopper was then inserted into the open end of the condenser and the nitrogen flow rate was reduced to approximately 0.5 liters/minute. The mixture was heated to $70°C$ for 16 hours. The conversion was quantitative.

The mixture was heated to $90°C$ and held at that temperature for 1 hour to destroy any residual V-601, then was cooled back to $70°C$. The nitrogen inlet tube was then removed, and 13.6 g of 95% DBTDL were added to the mixture, followed by 41.1 g of TMI. The TMI was added drop wise over the course of approximately 5 minutes while stirring the reaction mixture. The nitrogen inlet tube was replaced, the hollow glass stopper in the condenser was removed, and the reaction flask was purged with dry nitrogen for 30 minutes at a flow rate of approximately 2 liters/minute. The hollow glass stopper was reinserted into the open end of the condenser and the nitrogen flow rate was reduced to approximately 0.5 liters/minute. The mixture was allowed to react at $70°C$ for 6 hours, at which time the conversion was quantitative.

The mixture was then cooled to room temperature. The cooled mixture was a viscous, transparent liquid containing no visible insoluble mater. The percent solids of the liquid mixture was determined to be 24.80% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 150,600 Da and M_w/M_n of 2.6 based on two independent measurements. The product is a copolymer of LMA and

HEMA containing random side chains of TMI and is designed herein as LMA/HEMA-TMI (94/6-4.7% w/w) and suitable for making a gel organosol.

Example 3

Using the method and apparatus of Example 1, 475 g of Norpar^{TM} 12, 146 g of LMA, 17 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70°C for 16 hours. The mixture was then heated to 90°C for 1 hour to destroy any residual V-601, then was cooled back to 70°C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70°C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, slightly cloudy solution, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 24.83% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 160,200 Da and M_w/M_n of 2.8 based upon two independent measurements. The product is a copolymer of LMA and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA-TMI (90/10-4.7% w/w) and is suitable for making a gel organosol.

Example 4

Using the method and apparatus of Example 1, 474 g of Norpar^{TM} 12, 138 g of LMA, 25 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70°C for 16 hours. The mixture was then heated to 90°C for 1 hour to destroy any residual V-601, then was cooled back to 70°C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70°C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was an opaque dispersion, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 24.78% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the M_w of the copolymer was

too high to pass through the filter. The product is a copolymer of LMA and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA-TMI (85/15-4.7% w/w) and is suitable for making a gel organosol.

<div align="center">Example 5</div>

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 153 g of EHMA, 10 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, cloudy solution, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 25.27% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 138,100 Da and M_w/M_n of 2.3 based upon two independent measurements. The product is a copolymer of EHMA and HEMA containing random side chains of TMI and is designed herein as EHMA/HEMA-TMI (94/6-4.7% w/w) and is suitable for making a gel organosol.

<div align="center">Example 6</div>

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 153 g of TCHMA, 10 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, cloudy solution, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 26.47% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular

<div align="center">48</div>

weight was made using the GPC method described above; the copolymer had a M_w of 279,400 Da and M_w/M_n of 2.7 based upon two independent measurements. The product is a copolymer of TCHMA and HEMA containing random side chains of TMI and is designed herein as TCHMA/HEMA-TMI (94/6-4.7% w/w) and is suitable for making a gel organosol.

Example 7

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 146 g of ODA, 17 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, white opaque dispersion, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 25.45% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the M_w of the copolymer was too high to pass through the filter. The product is a copolymer of ODA and HEMA containing random side chains of TMI and is designed herein as ODA/HEMA-TMI (90/10-4.7% w/w) and is suitable for making a gel organosol.

Example 8

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 146 g of BHA, 17 g of 98% HEMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, white opaque dispersion, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 25.49% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the M_w of the copolymer was too high to pass through the filter. The product is a copolymer of BHA and HEMA containing random side chains of TMI and is designed herein as BHA/HEMA-TMI (90/10-4.7% w/w) and is suitable for making a gel organosol.

Example 9

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 155 g of LMA, 5 g of 98% HEMA, 2.5 g of MAA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, clear solution, containing no insoluble mater.

The percent solids of the liquid mixture was determined to be 24.23% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 146,600 Da and M_w/M_n of 2.4 based upon two independent measurements. The product is a copolymer of LMA, MAA and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA/MAA-TMI (95.5/3/1.5-4.7% w/w) and is suitable for making a gel organosol.

Example 10

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 155 g of TCHMA, 5 g of 98% HEMA, 2.5 g of MAA and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the

procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was clear gel, containing no insoluble mater.

The percent solids of the liquid mixture was determined to be 26.09% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 277,600 Da and M_w/M_n of 2.8 based upon two independent measurements. The product is a copolymer of TCHMA, MAA and HEMA containing random side chains of TMI and is designed herein as TCHMA/HEMA/MAA-TMI (95.5/3/1.5-4.7% w/w) and is suitable for making a gel organosol.

Example 11

Using the method and apparatus of Example 1, 475 g of Norpar™ 12, 153 g of LMA, 5 g of 98% HEMA, 4.9 g of AAM and 2.44 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was then heated to 90° C for 1 hour to destroy any residual V-601, then was cooled back to 70° C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70° C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was slightly cloudy solution, containing phase-separated polymer.

The percent solids of the liquid mixture was determined to be 24.78 % using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 160,300 Da and M_w/M_n of 1.6 based upon two independent measurements. The product is a copolymer of LMA, AAM and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA/AAM-TMI (94/3/3-4.7% w/w) and is suitable for making a gel organosol.

Example 12

Using the method and apparatus of Example 1, 475 g of Norpar^{TM} 12, 153 g of LMA, 5 g of 98% HEMA, 4.9 g of DAAM and 2.44 g of V-601 were combined and resulting mixture reacted at 70°C for 16 hours. The mixture was then heated to 90°C for
5   1 hour to destroy any residual V-601, then was cooled back to 70°C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the procedure of Example 1, the mixture was reacted at 70°C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, clear solution, containing no insoluble
10   mater.

The percent solids of the liquid mixture was determined to be 25.55% using the Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of 140,000 Da and M_w/M_n of 2.3 based upon two independent measurements. The product
15   is a copolymer of LMA, DAAM and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA/DAAM-TMI (94/3/3-4.7% w/w) and is suitable for making a gel organosol.

Example 13

20   Using the method and apparatus of Example 1, 475 g of Norpar^{TM} 12, 153 g of LMA, 5 g of 98% HEMA, 4.9 g of GMA and 2.44 g of V-601 were combined and resulting mixture reacted at 70°C for 16 hours. The mixture was then heated to 90°C for 1 hour to destroy any residual V-601, then was cooled back to 70°C. To the cooled mixture was then added 2.5 g of 95% DBTDL and 7.6 g of TMI. Following the
25   procedure of Example 1, the mixture was reacted at 70°C for approximately 6 hours at which time the reaction was quantitative. The mixture was then cooled to room temperature. The cooled mixture was viscous, clear solution, containing no insoluble mater.

The percent solids of the liquid mixture was determined to be 25.89% using the
30   Halogen Lamp Drying Method described above. Subsequent determination of molecular weight was made using the GPC method described above; the copolymer had a M_w of

139,000 Da and M_w/M_n of 2.1 based upon two independent measurements. The product is a copolymer of LMA, GMA and HEMA containing random side chains of TMI and is designed herein as LMA/HEMA/GMA-TMI (94/3/3-4.7% w/w) and is suitable for making a gel organosol.

5   The compositions of the graft stabilizers of Examples 1 -13 are summarized in the following table:

Table II, Graft Stabilizers

Example Number	Composition (%w/w)	Excess HEMA (wt %)	Appearance
1 (Comp.)	LMA/HEMA-TMI (97/3-4.7)	0	Clear solution, no insoluble polymer.
2	LMA/HEMA-TMI (94/6-4.7)	3	Clear solution, no insoluble polymer.
3	LMA/HEMA-TMI (90/10-4.7)	7	Cloudy solution, phase-separated polymer.
4	LMA/HEMA-TMI (85/15-4.7)	12	Opaque white dispersion
5	EHMA/HEMA-TMI (94/6-4.7)	3	Cloudy solution, phase-separated polymer.
6	TCHMA/HEMA-TMI (94/6-4.7)	3	Cloudy solution, phase-separated polymer.
7	ODA/HEMA-TMI (90/10-4.7)	7	Opaque white dispersion
8	BHA/HEMA-TMI (90/10-4.7)	7	Opaque white dispersion
9	LMA/HEMA/MAA-TMI (95.5/3/1.5-4.7)	1.5 (MAA)	Clear viscous solution, no insoluble polymer
10	TCHMA/HEMA/MAA-TMI (95.5/3/1.5-4.7)	1.5 (MAA)	Clear gel, no insoluble polymer
11	LMA/HEMA/AAM-TMI (94/3/3-4.7)	3 (AAM)	Slightly cloudy solution, phase-separated polymer.
12	LMA/HEMA/DAAM-TMI (94/3/3-4.7)	3 (DAAM)	Clear solution, no insoluble polymer.
13	LMA/HEMA/GMA-TMI (94/3/3-4.7)	3 (GMA)	Clear solution, no insoluble polymer.

10

Examples 14-30: Addition of D material to form organosols:

Example 14 (Comparative)

This is a comparative example using the graft stabilizer in Example 1 to prepare an organosol which did not gel. An 8 ounce (0.24 liter), narrow-mouthed glass bottle was charged with 126 g of Norpar™ 12, 14.6 g of EMA, 1.4 g of EA, 8.1 g of the graft stabilizer mixture from Example 1 at 24.72% polymer solids, and 0.18 g of V-601. The bottle was purged for 1 minute with dry nitrogen at a rate of approximately 1.5 liters/minute, then sealed with a screw cap fitted with a Teflon liner. The cap was secured in place using electrical tape. The sealed bottle was then inserted into a metal cage assembly and installed on the agitator assembly of an Atlas Launder-Ometer (Atlas Electric Devices Company, Chicago, IL). The Launder-Ometer was operated at its fixed agitation speed of 42 RPM with a water bath temperature of 70° C. The mixture was allowed to react for approximately 16-18 hours, at which time the conversion of monomer to polymer was quantitative. The mixture was cooled to room temperature, yielding an opaque white dispersion.

This organosol was designated LMA/HEMA-TMI//EA/EMA (97/3-4.7//13/87 %w/w). The percent solids of the organosol dispersion was determined to be 10.83% using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 0.25 μm.

Example 15

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 13.9 g of EMA, 1.3 g of EA, 0.8 g of 98% HEMA, 8.1 g of the graft stabilizer mixture from Example 1 at 24.72% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA-TMI//EA/EMA/HEMA (97/3-4.7//12.4/82.6/5 %w/w). The percent solids of the organosol dispersion was determined to be 10.19 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 35.7 μm.

Example 16

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 13.2 g of EMA, 1.2 g of EA, 1.4 g of 98% HEMA, 8.1 g of the graft stabilizer mixture from Example 1 at 24.72% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA-TMI//EA/EMA/HEMA (97/3-4.7//11.7/78.3/10 %w/w). The percent solids of the organosol dispersion was determined to be 8.73 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 62.7 μm.

Example 17

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 11.7 g of EMA, 1.1 g of EA, 2.6 g of 98% HEMA, 8.1 g of the graft stabilizer mixture from Example 1 at 24.72% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding a coagulated dispersion.

This organosol was designated LMA/HEMA-TMI//EA/EMA/HEMA (97/3-4.7//10.4/69.6/20 %w/w).

Example 18

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 14.6 g of EMA, 1.4 g of EA, 8.1 g of the graft stabilizer mixture from Example 3 at 24.83% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a weak gel.

This organosol was designated LMA/HEMA-TMI//EA/EMA (90/10-4.7//13/87 %w/w). The percent solids of the organosol dispersion was determined to be 10.59 % using the Halogen Lamp Drying Method described above. Subsequent determination of

average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 5.9 μm.

Example 19

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 14.6 g of EMA, 1.4 g of EA, 8.1 g of the graft stabilizer mixture from Example 4 at 24.78% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA-TMI//EA/EMA (85/15-4.7//13/87 %w/w). The percent solids of the organosol dispersion was determined to be 11.06 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 6.9 μm.

Example 20

A 5000 ml 3-neck round flask equipped with a condenser, a thermocouple connected to a digital temperature controller, a nitrogen inlet tube connected to a source of dry nitrogen and a magnetic stirrer, was charged with a mixture of 2945 g of Norpar™ 12, 315.1 g of EMA, 47.0 g of EA, 10.9 g of 98% HEMA, 188.2 g of the graft stabilizer mixture from Example 2 at 24.80 % polymer solids, and 4.20 g of V-601. While stirring the mixture, the reaction flask was purged with dry nitrogen for 30 minutes at flow rate of approximately 2 liters/minute. A hollow glass stopper was then inserted into the open end of the condenser and the nitrogen flow rate was reduced to approximately 0.5 liters/minute. The mixture was heated to 70° C for 16 hours. The conversion was quantitative. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

Approximately 350 g of n-heptane were added to the cooled organosol, and the resulting mixture was stripped of residual monomer using a rotary evaporator equipped with a dry ice/acetone condenser and operating at a temperature of 90° C and a vacuum of

approximately 15 mm Hg. The stripped organosol was cooled to room temperature, yielding an opaque white dispersion.

This organosol was designated LMA/HEMA-TMI//EA/EMA/HEMA (94/6-4.7//12.6/84.4/3 %w/w). The percent solids of the organosol dispersion after stripping was determined to be 12.24 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 128 μm.

Example 21

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 13.2 g of EMA, 1.2 g of EA, 1.4 g of 98% HEMA, 8.1 g of the graft stabilizer mixture from Example 3 at 24.78% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding coagulated dispersion.

This organosol was designated LMA/HEMA-TMI//EA/EMA/HEMA (94/6-4.7//11.7/78.3/10 %w/w).

Example 22

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 10.3 g of EMA, 4.9 g of EA, 0.8g of 98%HEMA, and 7.9g of the graft stabilizer mixture from Example 5 at 25.27% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a hard gel

This organosol was designated EHMA/HEMA-TMI//EA/EMA/HEMA (94/6-4.7//30.4/64.6/5 %w/w). The percent solids of the organosol dispersion was determined to be 11.72 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 7.5 μm.

Example 23

Using the method and apparatus of Example 14, 126 g of Norpar^{TM} 12, 10.8 g of EMA, 5.2 g of EA, 7.6 g of the graft stabilizer mixture from Example 6 at 26.47% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70°

5　　C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated TCHMA/HEMA-TMI//EA/EMA/HEMA (94/6-4.7//32/68 %w/w). The percent solids of the organosol dispersion was determined to be 11.44 % using the Halogen Lamp Drying Method described above. Subsequent

10　　determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 9.8 μm.

Example 24

Using the method and apparatus of Example 14, 126 g of Norpar^{TM} 12, 10.5 g of

15　　EMA, 5.0 g of EA, 0.5 g of 98%HEMA, 7.6 g of the graft stabilizer mixture from Example 6 at 26.47% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding a coagulated dispersion.

This organosol was designated TCHMA/HEMA-TMI//EA/EMA/HEMA (94/6-

20　　4.7//31/66/3 %w/w).

Example 25

Using the method and apparatus of Example 14, 126 g of Norpar^{TM} 12, 15.5 g of EMA, 0.5 g of 98% HEMA, 7.9 g of the graft stabilizer mixture from Example 7 at

25　　25.45% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated ODA/HEMA-TMI//EMA/HEMA (90/10-4.7//97/3 %w/w). The percent solids of the organosol dispersion was determined to be 6.62 %

30　　using the Halogen Lamp Drying Method described above. Subsequent determination of

average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 55.0 μm.

Example 26

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 15.5 g of EMA, 0.5 g of 98%HEMA, 7.8 g of the graft stabilizer mixture from Example 8 at 25.49% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated BHA/HEMA-TMI//EMA/HEMA (90/10-4.7//97/3 %w/w). The percent solids of the organosol dispersion was determined to be 8.43 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 66.2 μm.

Example 27

Using the method and apparatus of Example 14, 127 g of Norpar™ 12, 12.1 g of EMA, 3.5 g of EA, 0.5 g of 98% HEMA, 7.7 g of the graft stabilizer mixture from Example 10 at 26.09% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated TCHMA/HEMA/MAA-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3 %w/w). The percent solids of the organosol dispersion was determined to be 10.23 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 11.2 μm.

Example 28

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 12.1 g of EMA, 3.5 g of EA, 0.5 g of 98% HEMA, 8.1 g of the graft stabilizer mixture from Example 11 at 24.78% polymer solids, and 0.18 g of V-601 were combined and resulting

mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA/AAM-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3 %w/w). The percent solids of the organosol dispersion was determined to be 11.37 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 0.31 µm.

Example 29

Using the method and apparatus of Example 14, 126 g of Norpar™ 12, 12.0 g of EMA, 3.5 g of EA, 0.5 g of 98% HEMA, 7.8 g of the graft stabilizer mixture from Example 12 at 25.55% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA/DAAM-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3 %w/w). The percent solids of the organosol dispersion was determined to be 9.85 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 53.7 µm.

Example 30

Using the method and apparatus of Example 14, 127 g of Norpar™ 12, 12.1 g of EMA, 3.5 g of EA, 0.5 g of 98% HEMA, 7.7 g of the graft stabilizer mixture from Example 13 at 25.89% polymer solids, and 0.18 g of V-601 were combined and resulting mixture reacted at 70° C for 16 hours. The mixture was cooled to room temperature, yielding an opaque white dispersion which formed a gel.

This organosol was designated LMA/HEMA/GMA-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3 %w/w). The percent solids of the organosol dispersion was determined to be 11.65 % using the Halogen Lamp Drying Method described above. Subsequent determination of average particle size was made using the Laser Diffraction Analysis described above; the organosol had a volume average diameter of 29.5 µm.

The compositions of the organosols of Examples 14 -30 are summarized in the following table:

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Table III, Organosol Examples

Example Number	Composition (%w/w)	T_g of the D portion (°C)	HEMA in Shell/Core (wt %)	Physical Form
14 (Comp.)	LMA/HEMA-TMI// EA/EMA (97/3-4.7//13/87)	50	0/0	Non-gel
15	LMA/HEMA-TMI// EA/EMA/HEMA (97/3-4.7//12.4/82.6/5)	50	0/5	Gel
16	LMA/HEMA-TMI// EA/EMA/HEMA (97/3-4.7//11.7/78.3/10)	50	0/10	Gel
17	LMA/HEMA-TMI// EA/EMA/HEMA (97/3-4.7//10.4/69.6/20)	50	0/20	Coagulated
18	LMA/HEMA-TMI// EA/EMA (90/10-4.7//13/87)	50	7/0	Weak Gel
19	LMA/HEMA-TMI// EA/EMA (85/15-4.7//13/87)	50	12/0	Gel
20	LMA/HEMA-TMI// EA/EMA/HEMA (94/6-4.7//12.4/82.6/5)	50	3/3	Gel
21	LMA/HEMA-TMI// EA/EMA/HEMA (94/6-4.7//11.7/78.3/10)	50	3/10	Coagulated
22	EHMA/HEMA-TMI// EA/EMA/HEMA (94/6-4.7//30.4/64.6/5)	30	3/5	Hard Gel
23	TCHMA/HEMA-TMI// EA/EMA (94/6-4.7//32/68)	30	3/0	Gel
24	TCHMA/HEMA-TMI// EA/EMA/HEMA (94/6-4.7//31/66/3)	30	3/3	Coagulated

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25	ODA/HEMA-TMI// EMA/HEMA (90/10-4.7//97/3)	65	7/3	Gel
26	BHA/HEMA-TMI// EMA/HEMA (90/10-4.7//97/3)	65	7/3	Gel
27	TCHMA/HEMA/MAA-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3)	40	3(MAA)/3	Gel
28	LMA/HEMA/AAM-TMI// EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3)	40	3(AAM)/3	Gel
29	LMA/HEMA/DAAM-TMI//EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3)	40	3(DAAM)/3	Gel
30	LMA/HEMA/GMA-TMI// EA/EMA/HEMA (94/3/3-4.7//21.3/75.7/3)	40	3(GMA)/3	Gel

Examples 31-34: Preparation of Liquid Toners:

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Example 31

For characterization of the prepared liquid toner compositions in these Examples, the following were measured: size-related properties (particle size); charge-related properties (bulk and free phase conductivity, dynamic mobility and zeta potential); and charge/developed reflectance optical density (Z/ROD), a parameter that is directly

10   proportional to the toner charge/mass (Q/M).

This is an example of preparing a magenta liquid toner at a weight ratio of organosol copolymer to pigment of 5 (O/P ratio) using the organosol prepared in example 20, for which the weight ratio of D material to S material was 8. 245 g of the organosol at 12.24% (w/w) solids in Norpar™ 12 were combined with 48 g of Norpar™ 12, 6 g of

15   Pigment Red 81:4 (Magruder Color Company, Tucson, AZ) and 0.49 g of 6.11% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in an 8 ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Amex Co., Led., Tokyo, Japan) and charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at

2,000 RPM for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A 12% (w/w) solids toner concentrate exhibited the following properties as determined using the test methods described above:

5   Volume Mean Particle Size: 2.74 micron

Q/M: 66 μC/g

Bulk Conductivity: 133 picoMhos/cm

Percent Free Phase Conductivity: 6.4%

Dynamic Mobility: 6.89E-11 (m^2/Vsec).

10   This toner was tested using the printing procedure described above. The reflection optical density (ROD) was 1.34 at plating voltages greater than 525 volts. The printed image exhibited good electrostatic transfer properties with no flow pattern and background.

15   **Example 32**

This is an example of preparing a black liquid toner at a weight ratio of organosol copolymer to pigment of 6 (O/P ratio) using the organosol prepared in example 20, for which the weight ratio of D material to S material was 8. 252 g of the organosol at 12.24% (w/w) solids in Norpar™ 12 were combined with 42 g of Norpar™ 12, 5 g of

20 Black pigment (Aztech EK8200, Magruder Color Company, Tucson, AZ) and 0.42 g of 6.11% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in an 8 ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Amex Co., Led., Tokyo, Japan) and charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at

25 2,000 RPM for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A 12% (w/w) solids toner concentrate exhibited the following properties as determined using the test methods described above:

Volume Mean Particle Size: 3.04 micron

30 Q/M: 69μC/g

Bulk Conductivity: 117 picoMhos/cm

Percent Free Phase Conductivity: 11.3%

Dynamic Mobility: 4.02E-11 (m^2/Vsec).

This toner was tested using the printing procedure described above. The printed image made with this ink was poor with low reflection optical density (ROD) and flow pattern.

Example 33

This is an example of preparing a cyan liquid toner at a weight ratio of organosol copolymer to pigment of 6 (O/P ratio) using the organosol prepared in example 20, for which the weight ratio of D material to S material was 8. 252 g of the organosol at 12.24% (w/w) solids in Norpar™ 12 were combined with 42 g of Norpar™ 12, 5 g of Pigment Blue15:4 (PB:15:4, 249-3450, Sun Chemical Company, Cincinnati, Ohio) and 0.42 g of 6.11% Zirconium HEX-CEM solution (OMG Chemical Company, Cleveland, Ohio) in an 8 ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Amex Co., Led., Tokyo, Japan) and charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2,000 RPM for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

A 12% (w/w) solids toner concentrate exhibited the following properties as determined using the test methods described above:

Volume Mean Particle Size: 3.59 micron

Q/M: 72 μC/g

Bulk Conductivity: 14 picoMhos/cm

Percent Free Phase Conductivity: 2.7%

Dynamic Mobility: 1.45E-11 (m^2/Vsec).

This toner was tested using the printing procedure described above. The reflection optical density (ROD) was 0.58 at plating voltages greater than 525 volts.

Example 34

This is an example of preparing a yellow liquid toner at a weight ratio of organosol copolymer to pigment of 5 (O/P ratio) using the organosol prepared in example

20, for which the weight ratio of D material to S material was 8. 245 g of the organosol at 12.24% (w/w) solids in Norpar™ 12 were combined with 90 g of Norpar™ 12, 5.4 g of Pigment Yellow 138, 0.6 g of Pigment Yellow 83 (Sun Chemical Company, Cincinnati, Ohio) and 0.41 g of 6.11% Zirconium HEX-CEM solution (OMG Chemical

5 Company, Cleveland, Ohio) in an 8 ounce glass jar. This mixture was then milled in a 0.5 liter vertical bead mill (Model 6TSG-1/4, Amex Co., Led., Tokyo, Japan) and charged with 390 g of 1.3 mm diameter Potters glass beads (Potters Industries, Inc., Parsippany, NJ). The mill was operated at 2,000 RPM for 1.5 hours without cooling water circulating through the cooling jacket of the milling chamber.

10 A 12% (w/w) solids toner concentrate exhibited the following properties as determined using the test methods described above:

Volume Mean Particle Size: 3.49 micron

Q/M: 126 µC/g

Bulk Conductivity: 142 picoMhos/cm

15 Percent Free Phase Conductivity: 7.6%

Dynamic Mobility: 8.46E-11 (m^2/Vsec).

This toner was tested using the printing procedure described above. The reflection optical density (ROD) was 0.95 at plating voltages greater than 525 volts. The printed image exhibited good electrostatic transfer properties with no flow pattern and

20 background.

Toners are printed in an imaging system as described in 2003/0044202 at paragraphs 19-28 to evaluate image qualities on paper (such as optical density ("OD"), flow pattern, background, etc.), and transfer efficiencies (T0, T1, and T2). Ink solids are measured on the ITB. In the process, Scotch tape was used to pick ink particles from

25 various surfaces, such as OPC and ITB, and the taped images were placed on the blank paper to measure the ODs.

T0, T1 and T2 are defined as follows:
T0: inks are being transferred from developer roll to OPC

30 T1: inks are being transferred from OPC to ITB
T2: inks are being transferred from ITB to paper"

Table IV, Image Development and Transfer Characteristics of Hydrogen Bonding Gel Organosol Inks

	Example 31
T0 (tape)	1.723 OD
T1(-2.0KV) (tape)	94.9% remained OD 0.092
T2 (-2.5KV)	79.8%
T2 (-3.0KV)	72.8%
T2 (-4.0KV)	90.5%
T2 (-5.0KV)	89.1%
Paper OD @ -3.0KV	1.210 OD
ITB Ink % Solids	35.3%

5   Tested at 23 ^{0}C & 55% relative humidity   All Dev bias: 550/750 V

As shown in the table, excellent image transfer was observed in compositions of the present invention using an electrostatic image transfer process.

Other embodiments of this invention will be apparent to those skilled in the art

10   upon consideration of this specification or from practice of the invention disclosed herein. All patents, patent documents, and publications cited herein are incorporated by reference as if individually incorporated. Various omissions, modifications, and changes to the principles and embodiments described herein can be made by one skilled in the art without departing from the true scope and spirit of the invention which is indicated by the

15   following claims.